

Supplementary Information for

**Oxyboration With and Without a Catalyst: Borylated Isoxazoles via B–O  $\sigma$ -Bond Addition**

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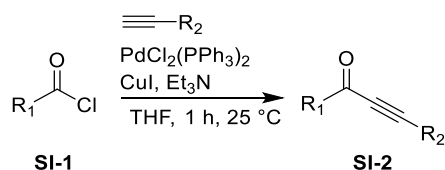
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## I. General Methods

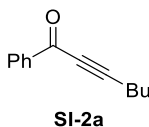
All reagents were used as received from commercial sources unless otherwise noted. Tetrahydrofuran, acetonitrile and triethylamine were dried by passing through an alumina column under argon pressure on a push still solvent system. Toluene-*d*<sub>8</sub> was dried over CaH<sub>2</sub>, degassed using three freeze-pump-thaw cycles, and vacuum transferred before use. Dioxane was degassed by sparging with nitrogen gas for 1 h. Manipulations were performed in a glovebox under nitrogen atmosphere unless otherwise noted. Analytical thin layer chromatography (TLC) was performed using Merck F<sub>250</sub> plates and visualized under UV irradiation at 254 nm, or using a basic aqueous solution of potassium permanganate. Flash chromatography was conducted using a Teledyne Isco Combiflash® Rf 200 Automatic Flash Chromatography System, and Teledyne Isco Redisep® 35–70 μm silica gel. All proton and carbon nuclear magnetic resonance (<sup>1</sup>H and <sup>13</sup>C NMR) spectra were recorded on a Bruker DRX-400 spectrometer, Bruker DRX-500 spectrometer outfitted with a cryoprobe, or a Bruker AVANCE-600 spectrometer. Boron nuclear magnetic resonance (<sup>11</sup>B NMR) spectra were recorded on a Bruker AVANCE-600 spectrometer. Fluorine nuclear magnetic resonance (<sup>19</sup>F NMR) spectra were recorded on a Bruker DRX-400 spectrometer. All coupling constants were measured in Hertz (Hz). Chemical shifts were reported in ppm and referenced to residual protonated solvent peak ( $\delta_{\text{H}} = 7.26$  ppm for CDCl<sub>3</sub>,  $\delta_{\text{H}} = 2.08$  ppm for *d*<sub>8</sub>-toluene,  $\delta_{\text{H}} = 2.05$  ppm for *d*<sub>6</sub>-acetone in <sup>1</sup>H NMR spectroscopy experiments;  $\delta_{\text{C}} = 77.16$  ppm for CDCl<sub>3</sub>,  $\delta_{\text{C}} = 20.43$  ppm for *d*<sub>8</sub>-toluene,  $\delta_{\text{C}} = 29.84$  ppm for *d*<sub>6</sub>-acetone in <sup>13</sup>C NMR spectroscopy experiments). <sup>11</sup>B and <sup>19</sup>F NMR spectroscopy experiments were referenced to the absolute frequency of 0 ppm in the <sup>1</sup>H dimension according to the Xi scale. High-resolution mass spectrometry data were obtained at the University of California, Irvine.

## II. Synthetic Procedures

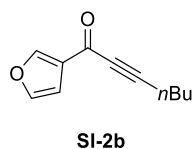
### A. Preparation of alkynyl ketone **SI-2(a-k)**. General procedure.



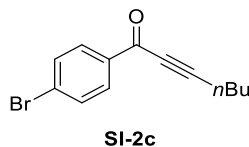
Ketones were prepared according to a literature procedure.<sup>1</sup> Using standard Schlenk line, to a flame-dried round bottom flask equipped with stir bar under N<sub>2</sub> atmosphere was added acid chloride **SI-1** (10.0 mmol, 1.00 equiv), PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (140 mg, 0.20 mmol, 2.0 mol %), CuI (76 mg, 0.40 mmol, 4.0 mol %), Et<sub>3</sub>N (1.39 mL, 10.0 mmol, 1.00 equiv), and alkyne (1.0 equiv) in dry THF (50 mL) at 25 °C. The resulting reaction mixture was stirred at room temperature for 1 h. The reaction was quenched with DI water (30 mL). The aqueous layer was extracted with EtOAc (3 × 30 mL). The combined organic layers were washed with brine (30 mL), dried over MgSO<sub>4</sub>, filtered, and concentrated in vacuo. The resulting crude solid was purified by silica gel flash column chromatography using an elution gradient from 100% hexanes to 10% EtOAc in hexanes. Product-containing fractions were combined and concentrated in vacuo to afford **SI-2**.



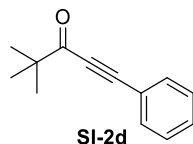
**1-phenylhept-2-yn-1-one (SI-2a)** was obtained as yellow oil (1.60 g, 86% isolated yield). TLC (20% EtOAc/hexanes): R<sub>f</sub> = 0.50, visualized by UV absorbance. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz): δ 8.15–8.13 (m, 2H), 7.61–7.58 (m, 1H), 7.49–7.46 (m, 2H), 2.51 (t, *J* = 7.0 Hz, 2H), 1.67 (quintet, *J* = 7.5 Hz, 2H), 1.52 (sextet, *J* = 7.5 Hz, 2H), 0.97 (t, *J* = 7.5 Hz, 3H). This spectrum is in agreement with previously reported spectral data.<sup>2</sup>



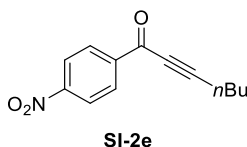
**1-(3-furyl)hept-2-yn-1-one (SI-2b)** was obtained as brown oil (1.53 g, 87% isolated yield). TLC (20% EtOAc/hexanes): R<sub>f</sub> = 0.47, visualized by UV absorbance. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz): δ 8.11 (s, 1H), 7.42 (s, 1H), 6.81 (s, 1H), 2.44 (t, *J* = 7.0 Hz, 2H), 1.63 (quintet, *J* = 7.0 Hz, 2H), 1.49 (sextet, *J* = 7.5 Hz, 2H), 0.95 (t, *J* = 7.5 Hz, 3H). This spectrum is in agreement with previously reported spectral data.<sup>3</sup>



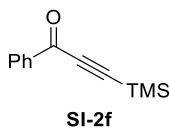
**1-(4-Bromophenyl)hept-2-yn-1-one (SI-2c)** was obtained as dark brown oil (2.31 g, 87% isolated yield). TLC (20% EtOAc/hexanes):  $R_f = 0.55$ , visualized by UV absorbance.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 500 MHz):  $\delta$  7.98 (d,  $J = 8.5$  Hz, 2H), 7.62 (d,  $J = 8.0$  Hz, 2H), 2.50 (t,  $J = 7.0$  Hz, 2H), 1.66 (quintet,  $J = 7.5$  Hz, 2H), 1.50 (sextet,  $J = 7.5$  Hz, 2H), 0.96 (t,  $J = 7.5$  Hz, 3H). This spectrum is in agreement with previously reported spectral data.<sup>4</sup>



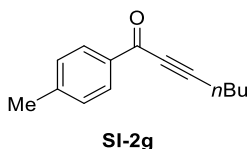
**1-Phenyl-4,4-dimethyl-pent-1-yn-3-one (SI-2d)** was obtained as yellow oil (1.35 g, 74% isolated yield). TLC (20% EtOAc/hexanes):  $R_f = 0.61$ , visualized by UV absorbance.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 500 MHz):  $\delta$  7.59–7.37 (m, 5H), 1.28 (s, 9H). This spectrum is in agreement with previously reported spectral data.<sup>5</sup>



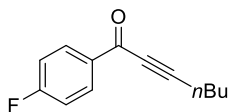
**1-(4-Nitrophenyl)hept-2-yn-1-one (SI-2e)** was obtained as reddish orange oil (1.76 g, 76% isolated yield). TLC (20% EtOAc/hexanes):  $R_f = 0.47$ , visualized by UV absorbance.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 600 MHz):  $\delta$  8.33–8.28 (m, 4H), 2.55 (t,  $J = 7.2$  Hz, 2H), 1.69 (quintet,  $J = 7.2$  Hz, 2H), 1.51 (sextet,  $J = 7.2$  Hz, 2H), 0.98 (t,  $J = 7.2$  Hz, 3H). This spectrum is in agreement with previously reported spectral data.<sup>6</sup>



**1-phenyl-3-trimethylsilyl-prop-2-yn-1-one (SI-2f)** was obtained as pale yellow oil (1.62 g, 80% isolated yield). TLC (20% EtOAc/hexanes):  $R_f = 0.67$ , visualized by UV absorbance.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 500 MHz):  $\delta$  8.15 (d,  $J = 7.0$  Hz, 2H), 7.62 (t,  $J = 7.0$  Hz, 1H), 7.49 (t,  $J = 7.0$  Hz, 2H), 0.32 (s, 9H). This spectrum is in agreement with previously reported spectral data.<sup>7</sup>

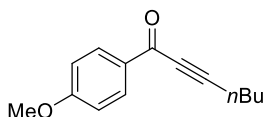


**1-(4-Methylphenyl)hept-2-yn-1-one (SI-2g)** was obtained as yellow oil (1.70 g, 85% isolated yield). TLC (20% EtOAc/hexanes):  $R_f = 0.52$ , visualized by UV absorbance.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 500 MHz):  $\delta$  8.03 (d,  $J = 8.5$  Hz, 2H), 7.27 (d,  $J = 9.0$  Hz, 2H), 2.50 (t,  $J = 7.0$  Hz, 2H), 2.43 (s, 3H), 1.66 (quintet,  $J = 7.5$  Hz, 2H), 1.50 (sextet,  $J = 7.5$  Hz, 2H), 0.96 (t,  $J = 7.5$  Hz, 3H). This spectrum is in agreement with previously reported spectral data.<sup>6</sup>



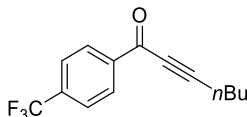
SI-2h

**1-(4-Fluorophenyl)hept-2-yn-1-one (SI-2h)** was obtained as yellow oil (1.51 g, 74% isolated yield). TLC (20% EtOAc/hexanes):  $R_f = 0.57$ , visualized by UV absorbance.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 500 MHz):  $\delta$  8.17–8.14 (m, 2H), 7.15 (t,  $J = 8.5$  Hz, 2H), 2.51 (t,  $J = 7.0$  Hz, 2H), 1.67 (quintet,  $J = 7.5$  Hz, 2H), 1.52 (sextet,  $J = 7.5$  Hz, 2H), 0.97 (t,  $J = 7.5$  Hz, 3H). This spectrum is in agreement with previously reported spectral data.<sup>8</sup>



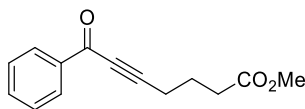
SI-2i

**1-(4-Methoxyphenyl)hept-2-yn-1-one (SI-2i)** was obtained as yellow oil (1.74 g, 81% isolated yield). TLC (20% EtOAc/hexanes):  $R_f = 0.38$ , visualized by UV absorbance.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 600 MHz):  $\delta$  8.10 (d,  $J = 9.0$  Hz, 2H), 6.94 (d,  $J = 8.4$  Hz, 2H), 3.88 (s, 3H), 2.49 (t,  $J = 7.2$  Hz, 2H), 1.66 (quintet,  $J = 7.2$  Hz, 2H), 1.50 (sext,  $J = 7.8$  Hz, 2H), 0.96 (t,  $J = 7.2$  Hz, 3H). This spectrum is in agreement with previously reported spectral data.<sup>6</sup>



SI-2j

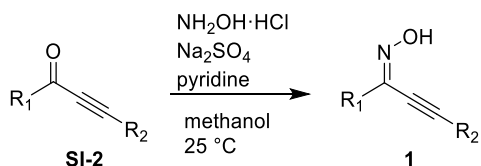
**1-(4-Trifluoromethylphenyl)hept-2-yn-1-one (SI-2j)** was obtained as dark yellow oil (2.19 g, 87% isolated yield). TLC (20% EtOAc/hexanes):  $R_f = 0.48$ , visualized by UV absorbance.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 500 MHz):  $\delta$  8.24 (d,  $J = 8.0$  Hz, 2H), 7.75 (d,  $J = 8.0$  Hz, 2H), 2.53 (t,  $J = 7.0$  Hz, 2H), 1.68 (quintet,  $J = 7.0$  Hz, 2H), 1.51 (sext,  $J = 7.5$  Hz, 2H), 0.97 (t,  $J = 7.5$  Hz, 3H). This spectrum is in agreement with previously reported spectral data.<sup>4</sup>



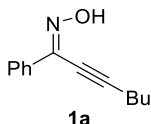
SI-2k

**Methyl 7-oxo-7-phenyl-hept-5-yn-1-oate (SI-2k)** was obtained as dark yellow solid (1.95 g, 85% isolated yield). TLC (20% EtOAc/hexanes):  $R_f = 0.22$ , visualized by UV absorbance.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 500 MHz):  $\delta$  8.12 (d,  $J = 8.0$  Hz, 2H), 7.61 (t,  $J = 7.5$  Hz, 1H), 7.48 (t,  $J = 7.5$  Hz, 2H), 3.70 (s, 3H), 2.60 (t,  $J = 7.0$  Hz, 2H), 2.53 (t,  $J = 7.0$  Hz, 2H), 2.01 (quintet,  $J = 7.0$  Hz, 2H).  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ , 125 MHz):  $\delta$  178.2, 173.3, 136.9, 134.1, 129.7, 128.7, 95.1, 80.3, 51.9, 32.8, 23.2, 18.8. HRMS (ESI+)  $m/z$  calcd for  $\text{C}_{14}\text{H}_{14}\text{O}_3$  ( $[\text{M}+\text{Na}]^+$ ) 253.0841, found 253.0832.

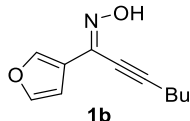
## B. Preparation of alkynyl oxime **1a–k**. General procedure.



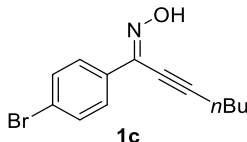
Oximes were prepared according to a literature procedure.<sup>9</sup> Open to air, a 50 mL round bottom flask was charged with H<sub>2</sub>NOH·HCl (2.2 equiv), Na<sub>2</sub>SO<sub>4</sub> (3.0 equiv), and a stir bar. The solids were suspended in MeOH (20 mL). Pyridine (4.0 equiv) and then ketone **SI-2** (1.0 equiv) were added. The reaction was allowed to stir at room temperature until the starting material was consumed completely, as shown by TLC after 5 h. The reaction was quenched with DI water (25 mL) and extracted with EtOAc (3 × 25 mL). The combined organic layers were washed with brine (25 mL), dried over MgSO<sub>4</sub>, filtered, and concentrated in vacuo. The crude was purified by silica gel flash column chromatography using a stepwise gradient from 5% to 10% EtOAc in hexanes. Product-containing fractions were combined and concentrated in vacuo to afford **1**.



**(Z)-1-phenylhept-2-yn-1-one oxime (1a)** was obtained as light yellow solid (38 mg, 22% isolated yield). TLC (20% EtOAc/hexanes): R<sub>f</sub> = 0.30, visualized by UV absorbance. <sup>1</sup>H NMR (*d*<sub>8</sub>-toluene, 500 MHz): δ 9.12 (s, 1H), 7.98 (d, *J* = 7.5 Hz, 2H), 7.12–7.05 (m, 3H), 2.16 (t, *J* = 7.0 Hz, 2H), 1.37–1.23 (m, 4H), 0.75 (t, *J* = 7.5 Hz, 3H). This spectrum is in agreement with previously reported spectral data.<sup>3</sup>

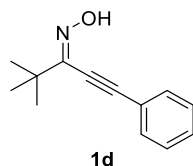


**(Z)-1-(3-furyl)hept-2-yn-1-one oxime (1b)** was obtained as yellow solid (115 mg, 6.9% isolated yield). TLC (20% EtOAc/hexanes): R<sub>f</sub> = 0.27, visualized by UV absorbance. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz): δ 7.85 (s, 1H), 7.74 (s, 1H), 7.39 (s, 1H), 6.69 (s, 1H), 2.52 (t, *J* = 7.0 Hz, 2H), 1.65 (quintet, *J* = 7.0 Hz, 2H), 1.50 (sextet, *J* = 7.5 Hz, 2H), 0.96 (t, *J* = 7.0 Hz, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz): δ 143.9, 143.3, 136.0, 122.4, 107.5, 102.9, 70.2, 30.4, 22.2, 19.4, 13.7. HRMS (ESI+) *m/z* calcd for C<sub>11</sub>H<sub>13</sub>NO<sub>2</sub> ([M+Na]<sup>+</sup>) 214.0844, found 214.0849.

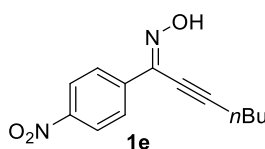


**(Z)-1-(4-Bromophenyl)hept-2-yn-1-one oxime (1c)** was obtained as brown solid (0.234 g, 9.6% isolated yield). TLC (20% EtOAc/hexanes): R<sub>f</sub> = 0.26, visualized by UV absorbance. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz): δ 8.34 (s, 1H), 7.69 (d, *J* = 8.6 Hz, 2H), 7.51 (d, *J* = 8.6 Hz, 2H), 2.58 (t, *J* = 7.1 Hz, 2H), 1.67 (quintet, *J* = 7.1 Hz, 2H), 1.51 (sextet, *J* = 7.5 Hz, 2H), 0.96 (t, *J* = 7.4 Hz, 3H).

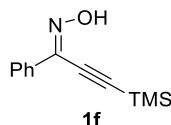
$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz):  $\delta$  141.6, 132.7, 131.7, 128.2, 124.3, 106.2, 70.2, 30.4, 22.2, 19.6, 13.7. HRMS (ESI+)  $m/z$  calcd for  $\text{C}_{13}\text{H}_{14}\text{BrNO}$  ( $[\text{M}+\text{Na}]^+$ ) 302.0157, found 302.0148.



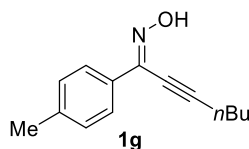
**(Z)-1-Phenyl-4,4-dimethylpent-1-yn-3-one oxime (1d)** was obtained as white solid (0.863 g, 58% isolated yield). TLC (20% EtOAc/hexanes):  $R_f = 0.38$ , visualized by UV absorbance.  $^1\text{H}$  NMR ( $d_8$ -toluene, 600 MHz):  $\delta$  9.58 (s, 1H), 7.37–7.36 (m, 2H), 6.97–6.90 (m, 3H), 1.23 (s, 9H). This spectrum is in agreement with previously reported spectral data.<sup>3</sup>



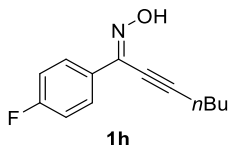
**(Z)-1-(4-Nitrophenyl)hept-2-yn-1-one oxime (1e)** was obtained as dark yellow solid (0.112 g, 6.0% isolated yield). TLC (20% EtOAc/hexanes):  $R_f = 0.26$ , visualized by UV absorbance.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 600 MHz):  $\delta$  8.20 (s, 1H), 8.14–8.13 (m, 2H), 7.91–7.89 (m, 2H), 2.50 (t,  $J = 7.2$  Hz, 2H), 1.59 (quintet,  $J = 7.3$  Hz, 2H), 1.42 (sextet,  $J = 7.5$  Hz, 2H), 0.88 (t,  $J = 7.4$  Hz, 3H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 150 MHz):  $\delta$  148.6, 140.8, 139.7, 127.4, 123.8, 107.2, 69.9, 30.3, 22.2, 19.6, 13.7. HRMS (ESI-)  $m/z$  calcd for  $\text{C}_{13}\text{H}_{14}\text{N}_2\text{O}_3$  ( $[\text{M}-\text{H}]^-$ ) 245.0926, found 245.0929.



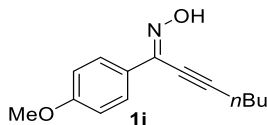
**(Z)-1-phenyl-3-trimethylsilyl-prop-2-yn-1-one oxime (1f)** was obtained as white solid (0.885 g, 51% isolated yield). TLC (20% EtOAc/hexanes):  $R_f = 0.41$ , visualized by UV absorbance.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz):  $\delta$  8.11 (s, 1H), 7.83–7.81 (m, 2H), 7.40–7.39 (m, 3H), 0.33 (s, 9H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz):  $\delta$  142.1, 133.1, 130.1, 128.6, 126.6, 110.4, 92.7, -0.19. HRMS (ESI+)  $m/z$  calcd for  $\text{C}_{12}\text{H}_{15}\text{NOSi}$  ( $[\text{M}+\text{Na}]^+$ ) 240.0821, found 240.0815.



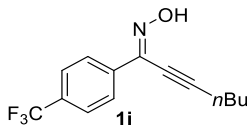
**(Z)-1-(4-Methylphenyl)hept-2-yn-1-one oxime (1g)** was obtained as light yellow solid (0.347 g, 19% isolated yield). TLC (20% EtOAc/hexanes):  $R_f = 0.34$ , visualized by UV absorbance.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz):  $\delta$  8.49 (s, 1H), 7.71 (d,  $J = 8.2$  Hz, 2H), 7.19 (d,  $J = 8.2$  Hz, 2H), 2.58 (t,  $J = 7.1$  Hz, 2H), 2.37 (s, 3H), 1.68 (quintet,  $J = 7.3$  Hz, 2H), 1.52 (sextet,  $J = 7.5$  Hz, 2H), 0.97 (t,  $J = 7.3$  Hz, 3H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz):  $\delta$  142.4, 140.1, 131.0, 129.5, 126.6, 105.5, 70.7, 30.5, 22.2, 21.5, 19.6, 13.7. HRMS (ESI+)  $m/z$  calcd for  $\text{C}_{14}\text{H}_{17}\text{NO}$  ( $[\text{M}+\text{Na}]^+$ ) 238.1208, found 238.1200.



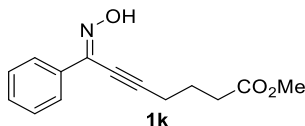
**(Z)-1-(4-Fluorophenyl)hept-2-yn-1-one oxime (1h)** was obtained as yellow oil (0.178 g, 11% isolated yield). TLC (20% EtOAc/hexanes):  $R_f = 0.29$ , visualized by UV absorbance.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  8.02 (s, 1H), 7.83–7.80 (m, 2H), 7.07 (t,  $J = 8.4$  Hz, 2H), 2.58 (t,  $J = 7.2$  Hz, 2H), 1.68 (quintet,  $J = 7.2$  Hz, 2H), 1.53 (sextet,  $J = 7.6$  Hz, 2H), 0.97 (t,  $J = 7.6$  Hz, 3H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz):  $\delta$  164.9, 162.9, 141.5, 129.85, 129.82, 128.57, 128.50, 115.65, 115.48, 106.0, 70.3, 30.4, 22.2, 19.6, 13.7.  $^{19}\text{F}$  NMR ( $\text{CDCl}_3$ , 376 MHz):  $\delta$  -111.2. HRMS (ESI+)  $m/z$  calcd for  $\text{C}_{13}\text{H}_{14}\text{FNO}$  ( $[\text{M}+\text{Na}]^+$ ) 242.0957, found 242.0957.



**(Z)-1-(4-Methoxyphenyl)hept-2-yn-1-one oxime (1i)** was obtained as yellow solid (0.318 g, 17% isolated yield). TLC (20% EtOAc/hexanes):  $R_f = 0.19$ , visualized by UV absorbance.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 600 MHz):  $\delta$  8.15 (s, 1H), 7.77–7.76 (m, 2H), 6.91–6.89 (m, 2H), 3.84 (s, 3H), 2.57 (t,  $J = 7.1$  Hz, 2H), 1.67 (quintet,  $J = 7.2$  Hz, 2H), 1.51 (sextet,  $J = 7.6$  Hz, 2H), 0.97 (t,  $J = 7.4$  Hz, 3H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz):  $\delta$  161.1, 142.1, 128.1, 126.4, 113.9, 105.4, 70.6, 55.5, 30.5, 22.2, 19.6, 13.7. HRMS (ESI+)  $m/z$  calcd for  $\text{C}_{14}\text{H}_{17}\text{NO}_2$  ( $[\text{M}+\text{Na}]^+$ ) 254.1157, found 254.1158.



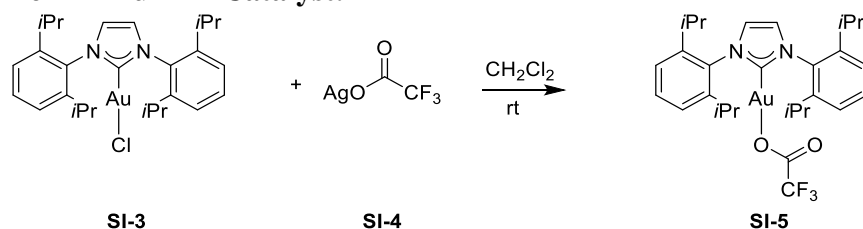
**(Z)-1-(4-Trifluoromethylphenyl)hept-2-yn-1-one oxime (1j)** was obtained as light brown solid (0.262 g, 11% isolated yield). TLC (20% EtOAc/hexanes):  $R_f = 0.32$ , visualized by UV absorbance.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz):  $\delta$  8.26 (s, 1H), 7.94 (d,  $J = 8.0$  Hz, 2H), 7.64 (d,  $J = 8.0$  Hz, 2H), 2.59 (t,  $J = 7.5$  Hz, 2H), 1.68 (quintet,  $J = 7.0$  Hz, 2H), 1.52 (sextet,  $J = 7.5$  Hz, 2H), 0.97 (t,  $J = 7.5$  Hz, 3H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz):  $\delta$  141.1, 137.0, 131.7, 131.5, 126.9, 125.5 (q,  $J = 15$  Hz), 123.0, 106.6, 70.0, 30, 4, 22.2, 19.6, 13.7.  $^{19}\text{F}$  NMR ( $\text{CDCl}_3$ , 376 MHz):  $\delta$  -62.8. HRMS (ESI+)  $m/z$  calcd for  $\text{C}_{14}\text{H}_{14}\text{F}_3\text{NO}$  ( $[\text{M}+\text{Na}]^+$ ) 292.0925, found 292.0920.



**Methyl 7-hydroxyimino-7-phenylhept-5-yn-1-oate (1k)** was obtained as light yellow solid (0.175 g, 8.4% isolated yield). TLC (20% EtOAc/hexanes):  $R_f = 0.21$ , visualized by UV absorbance.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz):  $\delta$  8.51 (s, 1H), 7.82–7.80 (m, 2H), 7.39–7.38 (m, 3H), 3.69 (s, 3H), 2.66 (t,  $J = 7.0$  Hz, 2H), 2.56 (t,  $J = 7.5$  Hz, 2H), 2.02 (quintet,  $J = 7.0$  Hz, 2H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz):  $\delta$  173.5, 133.5, 130.0, 129.0, 128.6, 126.6, 103.9, 85.6, 51.9, 32.9, 23.6, 19.3. HRMS (ESI+)  $m/z$  calcd for  $\text{C}_{14}\text{H}_{15}\text{NO}_3$  ( $[\text{M}+\text{Na}]^+$ ) 268.0950, found 268.0951.

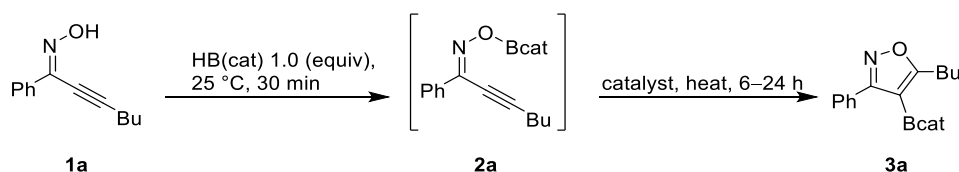


### C. Preparation of IPrAuTFA Catalyst.



No precautions were taken to exclude air or water. The reaction was conducted in a fume hood with the light turned off. A solution of IPrAuCl **SI-3** (124 mg, 200.  $\mu$ mol, 1.00 equiv) in DCM (2.0 mL) was added to a dram vial containing AgTFA **SI-4** (48.6 mg, 220.  $\mu$ mol, 1.10 equiv) and a stirbar. A white precipitation was observed. The vial was capped and wrapped with aluminum foil to protect the reaction mixture from light. The reaction was stirred vigorously at 25 °C for 7 h. The resulting suspension was then filtered through a Celite plug (ca. 0.5 mL). The Celite was rinsed with additional DCM (3  $\times$  0.5 mL), and the resulting solution was concentrated in vacuo to a white solid. The solid was crushed to a fine powder, from which volatiles were removed at 25 °C and ca. 10 mTorr for 18 h to afford IPrAuTFA **SI-5** as a white powder (135 mg, 97% isolated yield). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz):  $\delta$  7.53 (t,  $J$  = 7.8 Hz, 2H), 7.31 (d,  $J$  = 7.8 Hz, 4H), 7.21 (s, 2H), 2.53 (sept,  $J$  = 7.0 Hz, 4H), 1.35 (d,  $J$  = 7.0 Hz, 12H), 1.23 (d,  $J$  = 7.0 Hz, 12H). <sup>19</sup>F NMR (CDCl<sub>3</sub>, 376 MHz):  $\delta$  -74.1 (s). This spectrum is in agreement with previously reported spectral data.<sup>10</sup>

### D. Optimization of oxyboration reaction conditions.



**Boric ester 2a.** The reaction was performed inside N<sub>2</sub>-filled glovebox. A 4-dram vial was charged with a solution of **1a** (20.1 mg, 0.100 mmol, 1.00 equiv) in *d*<sub>8</sub>-toluene (0.30 mL). To this solution was added catecholborane (10.7  $\mu$ L, 0.100 mmol, 1.00 equiv) at 25 °C. The reaction mixture was stirred for 30 min during which the evolution of H<sub>2</sub> gas was observed, to afford **2a**, which was used directly in the screen of reaction conditions without further purification.

<sup>1</sup>H NMR (*d*<sub>8</sub>-toluene, 600 MHz):  $\delta$  8.10–8.09 (m, 2H), 7.12–7.10 (m, 3H), 6.91–6.90 (m, 2H), 6.72 (dd,  $J$  = 5.3, 3.4 Hz, 2H), 2.12 (t,  $J$  = 6.8 Hz, 2H), 1.35–1.28 (m, 4H), 0.79 (t,  $J$  = 7.1 Hz, 3H).

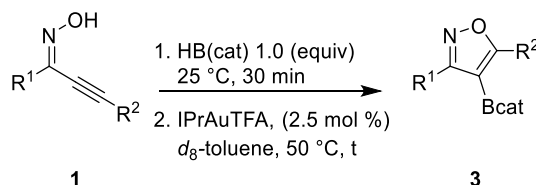
<sup>11</sup>B NMR (*d*<sub>8</sub>-toluene, 600 MHz):  $\delta$  25.4 (s).

**Boronic ester 3a.** Catalyst was dissolved in *d*<sub>8</sub>-toluene (0.2 mL) and added to the dram vial containing **2a**. After mixing thoroughly, the reaction mixture was transferred to a J. Young NMR tube, which was capped and removed from the glovebox. The tube was heated in a preheated oil bath at the temperature listed in Table SI-1. After heating for the indicated time, the progress of the reaction was monitored by <sup>1</sup>H and <sup>11</sup>B NMR spectroscopy.

$^1\text{H}$  NMR ( $d_8$ -toluene, 600 MHz):  $\delta$  7.92–7.90 (m, 2H), 7.26–7.19 (m, 3H), 6.92–6.90 (m, 2H), 3.26 (s, 3H), 6.76–6.74 (m, 2H), 2.97 (t,  $J$  = 7.6 Hz, 2H), 1.64 (quintet,  $J$  = 7.5 Hz, 2H), 1.28 (sextet,  $J$  = 7.4 Hz, 2H), 0.84 (t,  $J$  = 7.2 Hz, 3H).

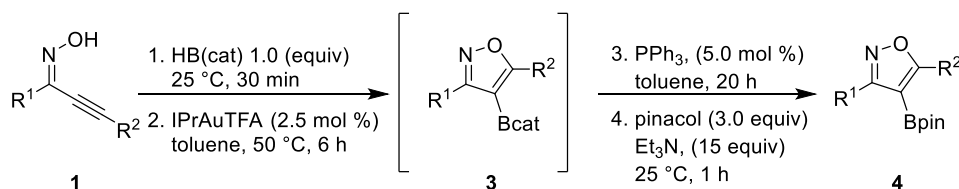
$^{11}\text{B}$  NMR ( $d_8$ -toluene, 600 MHz):  $\delta$  31.2 (s).

### E. General procedure NMR conversions using ERECTIC.



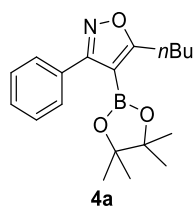
In a  $\text{N}_2$ -filled glovebox, an alkynyloxime (0.10 mmol, 1.0 equiv) was dissolved in 0.3 mL  $d_8$ -toluene in a 4-dram vial equipped with stir bar. Catecholborane (10.7  $\mu\text{L}$ , 0.100 mmol, 1.00 equiv) was added via gastight syringe to the solution above. The resulting solution was allowed to stir at room temperature for 0.5 h. The catalyst IPrAuTFA (1.8 mg, 0.0025 mmol, 2.5 mol %) was dissolved in 0.2 mL  $d_8$ -toluene and transferred via syringe to the solution above. This mixture was then transferred into a J. Young NMR tube, which was sealed and removed from the glove box. Reaction progress was monitored by  $^1\text{H}$  NMR spectroscopy (600 MHz,  $d_8$ -toluene) of **3** using the ERECTIC method relative to external mesitylene standard (252 mmol/L in  $d_8$ -toluene). This general procedure was used for  $\text{R}_1$  = Ph,  $\text{R}_2$  =  $n$ -Bu (**3a**, 90%, 6 h, 50  $^\circ\text{C}$ );  $\text{R}_1$  = 3-furyl,  $\text{R}_2$  =  $n$ -Bu (**3b**, 85%, 24 h, 50  $^\circ\text{C}$ );  $\text{R}_1$  = 4-BrC<sub>6</sub>H<sub>4</sub>,  $\text{R}_2$  =  $n$ -Bu (**3c**, 93%, 6 h, 50  $^\circ\text{C}$ );  $\text{R}_1$  =  $t$ -Bu,  $\text{R}_2$  = Ph (**3d**, 95%, 4 h, 110  $^\circ\text{C}$ );  $\text{R}_1$  = 4-NO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>,  $\text{R}_2$  =  $n$ -Bu (**3e**, 90%, 6 h, 50  $^\circ\text{C}$ );  $\text{R}_1$  = Ph,  $\text{R}_2$  = TMS (**3f**, 87%, 24 h, 90  $^\circ\text{C}$ );  $\text{R}_1$  = 4-MeC<sub>6</sub>H<sub>4</sub>,  $\text{R}_2$  =  $n$ -Bu (**3g**, 95%, 6 h, 50  $^\circ\text{C}$ );  $\text{R}_1$  = 4-FC<sub>6</sub>H<sub>4</sub>,  $\text{R}_2$  =  $n$ -Bu (**3h**, 92%, 6 h, 50  $^\circ\text{C}$ );  $\text{R}_1$  = 4-MeOC<sub>6</sub>H<sub>4</sub>,  $\text{R}_2$  =  $n$ -Bu (**3i**, 92%, 24 h, 60  $^\circ\text{C}$ );  $\text{R}_1$  = 4-CF<sub>3</sub>C<sub>6</sub>H<sub>4</sub>,  $\text{R}_2$  =  $n$ -Bu (**3j**, 98%, 6 h, 50  $^\circ\text{C}$ );  $\text{R}_1$  = Ph,  $\text{R}_2$  = (CH<sub>2</sub>)<sub>3</sub>CO<sub>2</sub>Me (**3k**, 94%, 8 h, 50  $^\circ\text{C}$ ).

### F. Synthesis of pinacol boronates 4: General procedure.

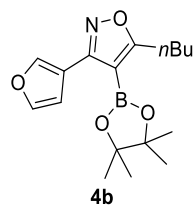


In a  $\text{N}_2$ -filled glovebox, oxime **1** (0.50 mmol, 1.0 equiv) was dissolved in 1.5 mL toluene in a 20-dram vial equipped with stir bar. Catecholborane (53.5  $\mu\text{L}$ , 0.500 mmol, 1.00 equiv) was added via gastight syringe to the solution above. The resulting solution was allowed to stir at room temperature for 0.5 h. The catalyst IPrAuTFA (8.8 mg, 0.012 mmol, 2.5 mol %) was dissolved in 1.0 mL toluene and transferred via syringe to the solution above in a capped vial and the resulting suspension was stirred in a pre-heated copper shot heating bath at appropriate temperature and time. The reaction mixture was then cooled to room temperature and a solution of PPh<sub>3</sub> (6.6 mg, 0.025 mmol, 5.0 mol %) in toluene (3.0 mL) was added. The resulting suspension was stirred for 20 h at room temperature in order to quench IPrAuTFA before proceeding.

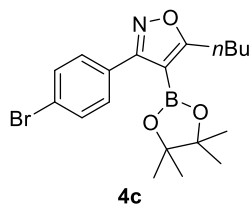
Pinacol (177 mg, 1.50 mmol, 3.00 equiv) was dissolved in anhydrous Et<sub>3</sub>N (1.04 mL, 7.50 mmol, 15.0 equiv). The resulting solution was added to the quenched reaction mixture, and the resulting suspension was stirred at 25 °C for 1 h. The reaction mixture was then removed from the glovebox. Volatiles were removed in vacuo. The resulting light brown oil was purified by silica gel chromatography using an elution gradient from 100% hexanes to 100% CH<sub>2</sub>Cl<sub>2</sub>. Solvents were removed in vacuo to afford the desired pinacol boronate **4**. All of the pinacol boronates **4a-4k** are missing one carbon signal in the <sup>13</sup>C NMR spectroscopy data. This carbon atom is assigned to the carbon in the newly formed C–B σ-bond. This is expected due to the quadrupolar relaxation of B.<sup>11</sup>



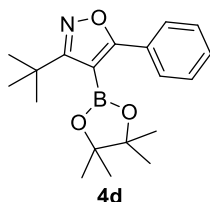
**Pinacol boronate (4a)** was obtained as clear oil at 50 °C after 6 h (0.123 g, 75% isolated yield). TLC (40% CH<sub>2</sub>Cl<sub>2</sub>/hexanes): R<sub>f</sub> = 0.10, visualized by UV absorbance. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 600 MHz): δ 7.82–7.80 (m, 2H), 7.41–7.40 (m, 3H), 3.00 (t, *J* = 7.8 Hz, 2H), 1.73 (quintet, *J* = 7.8 Hz, 2H), 1.40 (sextet, *J* = 7.8 Hz, 2H), 1.30 (s, 12H), 0.95 (t, *J* = 7.2 Hz, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz): δ 182.8, 166.1, 130.3, 129.4, 129.1, 128.1, 83.7, 30.7, 27.0, 24.9, 22.4, 13.8. <sup>11</sup>B NMR (CDCl<sub>3</sub>, 192 MHz): δ 29.9 (s). HRMS (ESI+) *m/z* calcd for C<sub>19</sub>H<sub>26</sub>BNO<sub>3</sub> ([M+Na]<sup>+</sup>) 350.1907, found 350.1903.



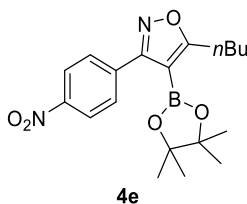
**Pinacol boronate (4b)** was obtained as clear oil at 50 °C after 24 h (0.113 g, 71% isolated yield). TLC (40% CH<sub>2</sub>Cl<sub>2</sub>/hexanes): R<sub>f</sub> = 0.09, visualized by UV absorbance. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz): δ 8.43 (s, 1H), 7.45–7.44 (m, 1H), 6.96 (s, 1H), 3.00 (t, *J* = 7.5 Hz, 2H), 1.69 (quintet, *J* = 7.5 Hz, 2H), 1.37 (sextet, *J* = 7.5 Hz, 2H), 1.34 (s, 12H), 0.93 (t, *J* = 7.5 Hz, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz): δ 183.6, 158.5, 144.3, 142.9, 116.3, 109.7, 83.8, 30.6, 26.8, 25.0, 22.3, 13.8. <sup>11</sup>B NMR (CDCl<sub>3</sub>, 192 MHz): δ 29.6 (s). HRMS (ESI+) *m/z* calcd for C<sub>17</sub>H<sub>24</sub>BNO<sub>4</sub> ([M+Na]<sup>+</sup>) 340.1699, found 340.1691.



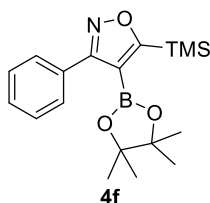
**Pinacol boronate (4c)** was obtained as yellow solid at 50 °C after 6 h (0.131 g, 65% isolated yield). TLC (40% CH<sub>2</sub>Cl<sub>2</sub>/hexanes): R<sub>f</sub> = 0.09, visualized by UV absorbance. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz): δ 7.71 (d, *J* = 8.5 Hz, 2H), 7.53 (d, *J* = 8.5 Hz, 2H), 3.00 (t, *J* = 7.5 Hz, 2H), 1.71 (quintet, *J* = 7.5 Hz, 2H), 1.41 (sextet, *J* = 7.0 Hz, 2H), 1.30 (s, 12H), 0.95 (t, *J* = 7.0 Hz, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz): δ 183.3, 165.2, 131.3, 130.7, 129.3, 123.8, 83.8, 30.6, 27.0, 24.9, 22.3, 13.8. <sup>11</sup>B NMR (CDCl<sub>3</sub>, 192 MHz): δ 29.7 (s). HRMS (ESI+) *m/z* calcd for C<sub>19</sub>H<sub>25</sub>BBrNO<sub>3</sub> ([M+H]<sup>+</sup>) 408.1175, found 408.1163.



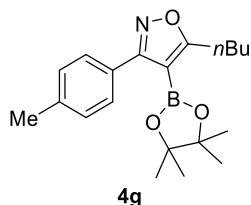
**Pinacol boronate (4d)** was obtained as white solid at 110 °C after 4 h (0.154 g, 94% isolated yield). TLC (40% CH<sub>2</sub>Cl<sub>2</sub>/hexanes): R<sub>f</sub> = 0.11, visualized by UV absorbance. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 600 MHz): δ 7.78–7.76 (m, 2H), 7.42–7.41 (m, 3H), 1.44 (s, 9H), 1.34 (s, 12H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz): δ 175.4, 174.7, 130.1, 129.1, 128.3, 125.8, 84.3, 33.4, 29.5, 25.1. <sup>11</sup>B NMR (CDCl<sub>3</sub>, 192 MHz): δ 30.5 (s). HRMS (ESI+) *m/z* calcd for C<sub>19</sub>H<sub>26</sub>BNO<sub>3</sub> ([M+H]<sup>+</sup>) 328.2088, found 328.2091.



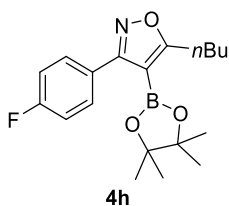
**Pinacol boronate (4e)** was obtained as light yellow solid at 50 °C after 6 h (0.112 g, 60% isolated yield). TLC (40% CH<sub>2</sub>Cl<sub>2</sub>/hexanes): R<sub>f</sub> = 0.10, visualized by UV absorbance. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz): δ 8.27 (d, *J* = 9.0 Hz, 2H), 8.03 (d, *J* = 8.5 Hz, 2H), 3.04 (t, *J* = 7.5 Hz, 2H), 1.73 (quintet, *J* = 7.0 Hz, 2H), 1.40 (sextet, *J* = 7.0 Hz, 2H), 1.31 (s, 12H), 0.96 (t, *J* = 7.5 Hz, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz): δ 184.0, 164.4, 148.5, 136.8, 130.1, 123.3, 84.0, 30.6, 27.0, 24.9, 22.3, 13.8. <sup>11</sup>B NMR (CDCl<sub>3</sub>, 192 MHz): δ 29.5 (s). HRMS (ESI+) *m/z* calcd for C<sub>19</sub>H<sub>25</sub>BN<sub>2</sub>O<sub>5</sub> ([M+Na]<sup>+</sup>) 395.1758, found 395.1760.



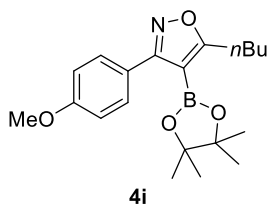
**Pinacol boronate (4f)** was obtained as white solid at 90 °C after 24 h (0.122 g, 71% isolated yield). TLC (40% CH<sub>2</sub>Cl<sub>2</sub>/hexanes): R<sub>f</sub> = 0.15, visualized by UV absorbance. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz): δ 7.78–7.76 (m, 2H), 7.41–7.40 (m, 3H), 1.30 (s, 12H), 0.43 (s, 9H). This spectrum is in agreement with previously reported spectral data.<sup>12</sup>



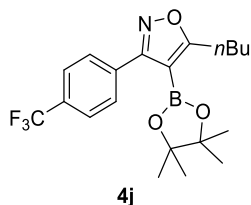
**Pinacol boronate (4g)** was obtained as light yellow solid at 50 °C after 6 h (0.128 g, 75% isolated yield). TLC (40% CH<sub>2</sub>Cl<sub>2</sub>/hexanes): R<sub>f</sub> = 0.14, visualized by UV absorbance. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz): δ 7.71 (d, *J* = 8.0 Hz, 2H), 7.21 (d, *J* = 8.0 Hz, 2H), 2.99 (t, *J* = 7.5 Hz, 2H), 2.39 (s, 3H), 1.72 (quintet, *J* = 7.5 Hz, 2H), 1.39 (sextet, *J* = 7.5 Hz, 2H), 1.30 (s, 12H), 0.95 (t, *J* = 7.5 Hz, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz): δ 182.7, 166.0, 139.3, 128.92, 128.87, 127.4, 83.7, 30.7, 27.0, 24.9, 22.4, 21.5, 13.8. <sup>11</sup>B NMR (CDCl<sub>3</sub>, 192 MHz): δ 29.9 (s). HRMS (ESI+) *m/z* calcd for C<sub>20</sub>H<sub>28</sub>BNO<sub>3</sub> ([M+H]<sup>+</sup>) 342.2244, found 342.2241.



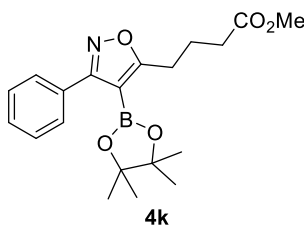
**Pinacol boronate (4h)** was obtained as clear oil at 50 °C after 6 h (0.115 g, 67% isolated yield). TLC (40% CH<sub>2</sub>Cl<sub>2</sub>/hexanes): R<sub>f</sub> = 0.11, visualized by UV absorbance. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz): δ 7.83–7.80 (m, 2H), 7.09 (t, *J* = 8.7 Hz, 2H), 3.00 (t, *J* = 7.5 Hz, 2H), 1.72 (quintet, *J* = 7.4 Hz, 2H), 1.40 (sextet, *J* = 7.5 Hz, 2H), 1.30 (s, 12H), 0.95 (t, *J* = 7.3 Hz, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz): δ 183.2, 165.3, 164.7, 162.7, 131.0, 126.4, 115.1, 83.8, 30.6, 27.0, 24.9, 22.4, 13.8. <sup>11</sup>B NMR (CDCl<sub>3</sub>, 192 MHz): δ 29.8 (s). <sup>19</sup>F NMR (CDCl<sub>3</sub>, 376 MHz): δ -112.3. HRMS (ESI+) *m/z* calcd for C<sub>19</sub>H<sub>25</sub>BFNO<sub>3</sub> ([M+Na]<sup>+</sup>) 368.1813, found 368.1802.



**Pinacol boronate (4i)** was obtained as off white solid at 60 °C after 24 h (0.132 g, 74% isolated yield). TLC (40% CH<sub>2</sub>Cl<sub>2</sub>/hexanes): R<sub>f</sub> = 0.23, visualized by UV absorbance. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 600 MHz): δ 7.79 (d, *J* = 8.8 Hz, 2H), 6.92 (d, *J* = 8.8 Hz, 2H), 3.83 (s, 3H), 2.99 (t, *J* = 7.5 Hz, 2H), 1.72 (quintet, *J* = 7.6 Hz, 2H), 1.39 (sextet, *J* = 7.4 Hz, 2H), 1.30 (s, 12H), 0.95 (t, *J* = 7.3 Hz, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz): δ 182.8, 165.7, 160.6, 130.4, 122.8, 113.5, 83.7, 55.4, 30.7, 27.0, 24.9, 22.4, 13.8. <sup>11</sup>B NMR (CDCl<sub>3</sub>, 192 MHz): δ 29.8 (s). HRMS (ESI+) *m/z* calcd for C<sub>20</sub>H<sub>28</sub>BNO<sub>4</sub> ([M+Na]<sup>+</sup>) 380.2013, found 380.2002.

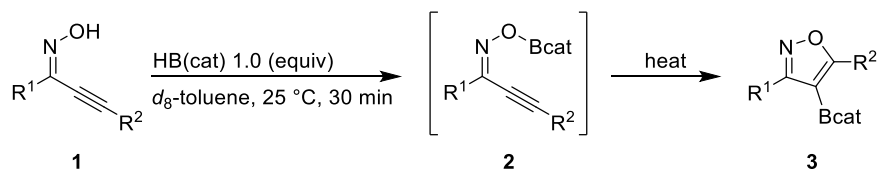


**Pinacol boronate (4j)** was obtained as off white solid at 50 °C after 6 h (0.110 g, 56% isolated yield). TLC (40% CH<sub>2</sub>Cl<sub>2</sub>/hexanes): R<sub>f</sub> = 0.15, visualized by UV absorbance. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 600 MHz): δ 7.96 (d, *J* = 8.4 Hz, 2H), 7.66 (d, *J* = 8.4 Hz, 2H), 3.03 (t, *J* = 7.8 Hz, 2H), 1.73 (quintet, *J* = 7.2 Hz, 2H), 1.41 (sextet, *J* = 7.8 Hz, 2H), 1.30 (s, 12H), 0.96 (t, *J* = 7.8 Hz, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz): δ 183.6, 165.1, 133.9, 131.4, 131.2, 129.5, 125.1 (q, *J* = 15.5 Hz), 123.2, 83.9, 30.6, 27.0, 24.9, 22.4, 13.8. <sup>11</sup>B NMR (CDCl<sub>3</sub>, 192 MHz): δ 29.7 (s). <sup>19</sup>F NMR (CDCl<sub>3</sub>, 376 MHz): δ -62.7. HRMS (ESI+) *m/z* calcd for C<sub>20</sub>H<sub>25</sub>BF<sub>3</sub>NO<sub>3</sub> ([M+H]<sup>+</sup>) 396.1962, found 396.1970.



**Pinacol boronate (4k)** was obtained as clear oil at 50 °C after 8 h (0.119 g, 64% isolated yield). TLC (100% CH<sub>2</sub>Cl<sub>2</sub>): R<sub>f</sub> = 0.28, visualized by UV absorbance. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 600 MHz): δ 7.81–7.80 (m, 2H), 7.42–7.38 (m, 3H), 3.67 (s, 3H), 3.07 (t, *J* = 7.8 Hz, 2H), 2.40 (t, *J* = 7.8 Hz, 2H), 2.09 (quintet, *J* = 7.2 Hz, 2H), 1.30 (s, 12H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz): δ 181.4, 173.5, 16.2, 130.0, 129.5, 129.1, 128.1, 83.9, 51.7, 33.3, 26.6, 24.9, 23.6. <sup>11</sup>B NMR (CDCl<sub>3</sub>, 192 MHz): δ 29.7 (s). HRMS (ESI+) *m/z* calcd for C<sub>20</sub>H<sub>26</sub>BNO<sub>5</sub> ([M+H]<sup>+</sup>) 372.1986, found 372.1983.

### G. Uncatalyzed Oxyboration.

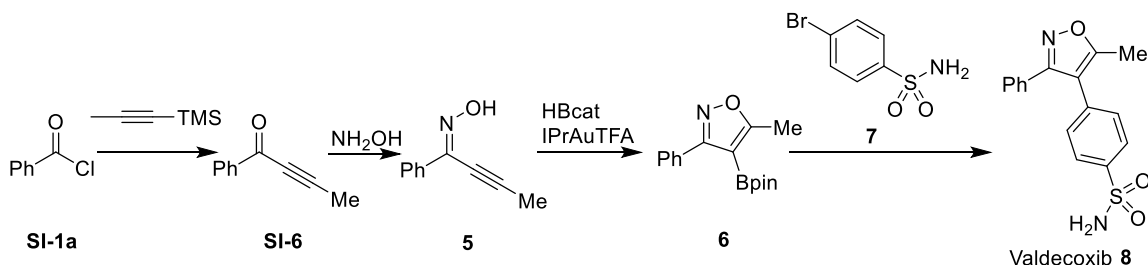


In a N<sub>2</sub>-filled glovebox, oxime **1** (0.10 mmol, 1.0 equiv) was dissolved in 0.5 mL *d*<sub>8</sub>-toluene in a 4-dram vial equipped with stir bar. Catecholborane (10.7 μL, 0.100 mmol, 1.00 equiv) was added via gastight syringe to the solution above. The resulting solution was allowed to stir at room temperature for 0.5 h. The reaction mixture was transferred via syringe to a J. Young NMR tube, removed from the glovebox, and heated in a preheated oil bath at 110 °C until full consumption of starting materials was achieved, after which the <sup>1</sup>H NMR yields were recorded. The <sup>1</sup>H NMR yields were determined by the ERECTIC method using mesitylene as the external standard.

**Table SI-1.** Uncatalyzed Oxyboration

	R <sup>1</sup> /R <sup>2</sup>	uncatalyzed <sup>1</sup> H NMR yield	time
<b>3a</b>	Ph/ <i>n</i> -Bu	89%	111 h
<b>3b</b>	3-Furyl/ <i>n</i> -Bu	68%	18 days
<b>3c</b>	4-BrC <sub>6</sub> H <sub>4</sub> / <i>n</i> -Bu	91%	20 h
<b>3d</b>	<i>t</i> -Bu/Ph	24%	7 days
<b>3e</b>	4-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> / <i>n</i> -Bu	84%	20 h
<b>3f</b>	Ph/TMS	0%	48 h
<b>3g</b>	4-MeC <sub>6</sub> H <sub>4</sub> / <i>n</i> -Bu	78%	15 days
<b>3h</b>	4-FC <sub>6</sub> H <sub>4</sub> / <i>n</i> -Bu	87%	65 h
<b>3i</b>	4-MeOC <sub>6</sub> H <sub>4</sub> / <i>n</i> -Bu	90%	65 h
<b>3j</b>	4-CF <sub>3</sub> C <sub>6</sub> H <sub>4</sub> / <i>n</i> -Bu	74%	21 days
<b>3k</b>	Ph/(CH <sub>2</sub> ) <sub>3</sub> CO <sub>2</sub> Me	83%	52 h

## H. Synthesis of Valdecoxib and Valdecoxib Ester Analog.



**1-phenylbut-2-yn-1-one (SI-6)** was prepared according to a literature procedure.<sup>15</sup> To a flame-dried 100 mL round bottom flask equipped with stir bar under N<sub>2</sub> atmosphere was added FeCl<sub>3</sub> (162 mg, 1.00 mmol, 0.10 equiv). The flask was evacuated and purged with N<sub>2</sub> in three cycles. The reaction flask was cooled to 0 °C in an ice-water bath. Acid chloride **SI-1a** (1.16 mL, 10.0 mmol, 1.00 equiv), trimethylsilylpropyne (2.22 mL, 15.0 mmol, 1.50 equiv), and CH<sub>3</sub>NO<sub>2</sub> (20.0 mL) were added to the reaction flask at 0 °C under N<sub>2</sub> atmosphere. The reaction mixture was stirred at 0 °C for 6 h. The reaction mixture was then allowed to warm to 25 °C. The suspension was filtered through a Celite plug (ca. 0.5 mL), and rinsed with dichloromethane (3 × 5 mL). The crude reaction mixture was concentrated in vacuo, purified by silica gel flash column chromatography (5% EtOAc in hexanes) to afford **SI-6** as a yellow oil (0.867 g, 60% isolated yield). TLC (20% EtOAc/hexanes): R<sub>f</sub> = 0.42, visualized by UV absorbance. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz) δ: 8.14 (d, *J* = 7.5 Hz, 2H), 7.60 (t, *J* = 7.5 Hz, 1H), 7.48 (t, *J* = 8.0 Hz, 2H), 2.16 (s, 3H). This spectrum is in agreement with previously reported spectral data.<sup>15</sup>

**(Z)-1-phenylbut-2-yn-1-one oxime (5)** was prepared according to a literature procedure.<sup>9</sup> A 50 mL round bottom flask was charged with H<sub>2</sub>NOH·HCl (2.2 equiv), Na<sub>2</sub>SO<sub>4</sub> (3.0 equiv), and a stir bar. The solids were suspended in MeOH (10 mL). Pyridine (4.0 equiv) and then ketone **SI-6** (1.0 equiv) were added. The reaction was stirred at room temperature until the starting material was consumed completely, as shown by TLC. The reaction was quenched with 15 mL DI water and extracted with EtOAc (3 × 15 mL). The combined organic layers were washed with brine (15 mL), dried over MgSO<sub>4</sub>, filtered, and concentrated in vacuo. The crude was purified by silica gel flash column chromatography using a stepwise gradient from 5% to 10% EtOAc in hexanes. Product-containing fractions were combined and concentrated in vacuo to afford **5** as a yellow solid (111 mg, 12% isolated yield). TLC (20% EtOAc/hexanes): R<sub>f</sub> = 0.19, visualized by UV absorbance. <sup>1</sup>H NMR (*d*<sub>8</sub>-toluene, 500 MHz): δ 9.03 (s, 1H), 7.95–7.93 (m, 2H), 7.11–7.06 (m, 3H), 1.61 (s, 3H). <sup>13</sup>C NMR (*d*<sub>8</sub>-toluene, 125 MHz): δ 142.1, 134.4, 129.7, 128.6, 126.9, 100.5, 71.0, 4.1. HRMS (ESI+) *m/z* calcd for C<sub>10</sub>H<sub>9</sub>NO ([M+Na]<sup>+</sup>) 182.0582, found 182.0579.

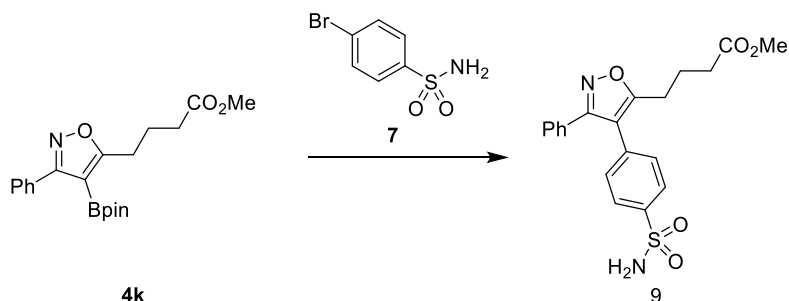
**Pinacol boronate (6)**. In a N<sub>2</sub>-filled glovebox, alkynyloxime **5** (31.8 mg, 0.200 mmol, 1.00 equiv) was dissolved in 0.6 mL toluene in a 4-dram vial equipped with stir bar. Catecholborane (21.4 μL, 0.200 mmol, 1.00 equiv) was added via gastight syringe to the solution above. The resulting solution was allowed to stir at room temperature for 0.5 h. The catalyst IPrAuTFA (3.5 mg, 0.0050 mmol, 2.5 mol %) was dissolved in 0.4 mL toluene and transferred via syringe to the solution above in a capped vial and the resulting suspension was stirred in a pre-heated 50 °C copper shot heating bath for 6 h. The reaction mixture was then cooled to room temperature and a solution of PPh<sub>3</sub> (2.6 mg, 0.010 mmol, 5.0 mol %) in toluene (1.2 mL) was added. The resulting suspension was stirred for 20 h at room temperature in order to quench IPrAuTFA before proceeding.

Pinacol (70.8 mg, 0.600 mmol, 3.00 equiv) was dissolved in anhydrous Et<sub>3</sub>N (0.42 mL, 3.0 mmol, 15.0 equiv). The resulting solution was added to the quenched reaction mixture, and the resulting suspension was stirred at 25 °C for 1 h. The reaction mixture was then removed from the glovebox. Volatiles were removed in vacuo. The resulting light brown oil was purified by silica gel chromatography using an elution gradient from 100% hexanes to 100% CH<sub>2</sub>Cl<sub>2</sub>. Solvents were removed in vacuo to afford the desired pinacol boronate **6** as white solid (40.5 mg, 71% isolated yield). TLC (40% CH<sub>2</sub>Cl<sub>2</sub>/hexanes): R<sub>f</sub> = 0.08, visualized by UV absorbance. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 600 MHz): δ 7.83–7.81 (m, 2H), 7.43–7.39 (m, 3H), 2.61 (s, 3H), 1.30(s, 12H). This spectrum is in agreement with previously reported spectral data.<sup>12</sup>

**Valdecoxib (8)** was prepared according to a literature procedure, but with using building block **6** from our method.<sup>123</sup> To a flame-dried 10 mL round bottom flask equipped with stir bar under N<sub>2</sub> atmosphere was added pinacol boronate **6** (54.4 mg, 0.191 mmol, 1.00 equiv), PdCl<sub>2</sub>(dppf)·DCM (15.5 mg, 0.0190 mmol, 0.100 equiv), K<sub>3</sub>PO<sub>4</sub> (122 mg, 0.574 mmol, 3.00 equiv), sulfonamide **7** (90.2 mg, 0.382 mmol, 2.00 equiv), and degassed dioxane (1.2 mL). The reaction mixture was stirred at 85 °C for 21 h. The reaction mixture was allowed to cool to 25 °C, quenched by DI water (10 mL). The aqueous layer was extracted with dichloromethane (3 × 20 mL). The combined organic layer was washed with brine (20 mL), dried over MgSO<sub>4</sub>, filtered, and concentrated in vacuo. The crude was purified by silica gel flash column chromatography using an elution gradient from 30% to 40% EtOAc in hexanes to afford **8** as a light yellow solid (37.4 mg, 62% isolated yield). TLC (40% EtOAc/hexanes): R<sub>f</sub> = 0.14, visualized by UV absorbance. <sup>1</sup>H NMR (CD<sub>3</sub>OD,

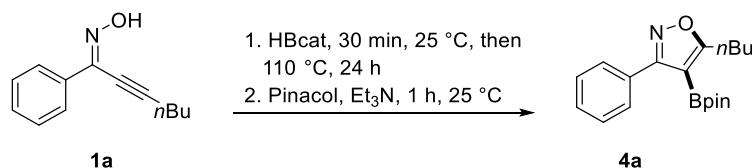


600 MHz)  $\delta$ : 7.91 (d,  $J$  = 8.4 Hz, 2H), 7.44–7.35 (m, 7H), 4.84 (s, 2H), 2.49 (s, 3H). This spectrum is in agreement with previously reported spectral data.<sup>12</sup>



**Valdecoxib ester analog (9)** was prepared according to a literature procedure,<sup>12</sup> using building block **4k** from our method. To a flame-dried 10 mL round bottom flask equipped with stir bar under N<sub>2</sub> atmosphere was added pinacol boronate **4k** (59.0 mg, 0.159 mmol, 1.00 equiv), PdCl<sub>2</sub>(dppf)·DCM (13.0 mg, 0.0159 mmol, 0.100 equiv), K<sub>3</sub>PO<sub>4</sub> (101 mg, 0.477 mmol, 3.00 equiv), sulfonamide **7** (75.0 mg, 0.318 mmol, 2.00 equiv), and degassed dioxane (1.20 mL). The reaction mixture was stirred at 90 °C for 46 h. The reaction mixture was allowed to cool to 25 °C, quenched by DI water (10 mL). The aqueous layer was extracted with dichloromethane (3 × 20 mL). The combined organic layer was washed with brine (20 mL), dried over MgSO<sub>4</sub>, filtered, and concentrated in vacuo. The crude was purified by silica gel flash column chromatography using an elution gradient from 30% to 40% EtOAc in hexanes to afford **9** as a white solid (47.1 mg, 74% isolated yield). TLC (40% EtOAc/hexanes): R<sub>f</sub> = 0.14, visualized by UV absorbance. <sup>1</sup>H NMR (*d*<sub>6</sub>-acetone, 500 MHz)  $\delta$ : 7.93–7.91 (m, 2H), 7.45–7.36 (m, 7H), 6.70 (bs, 1H), 3.81 (bs, 1H), 3.57 (s, 3H), 2.94–2.91 (m, 4H), 2.40 (t,  $J$  = 7.0 Hz, 2H). <sup>13</sup>C NMR (*d*<sub>6</sub>-acetone, 125 MHz):  $\delta$  173.3, 170.8, 161.6, 144.3, 134.8, 131.2, 130.3, 129.8, 129.4, 129.1, 127.2, 115.5, 51.6, 33.2, 25.4, 23.5. HRMS (ESI+)  $m/z$  calcd for C<sub>20</sub>H<sub>20</sub>N<sub>2</sub>O<sub>5</sub>S ([M+Na]<sup>+</sup>) 423.0991, found 423.0987.

#### L. Gram-scale preparation of 4a



The gram-scale uncatalyzed oxyboration reaction was conducted in a 100 mL Schlenk bomb equipped with stir bar under N<sub>2</sub> atmosphere. A flame-dried 100-mL Schlenk bomb with a stir bar was charged with oxime **1a** (1.47 g, 7.31 mmol, 1.00 equiv). Anhydrous toluene (7.3 mL) was added. To the resulting rapidly stirring suspension was added catecholborane (0.78 mL, 7.31 mmol, 1.00 equiv) via syringe, and allowed to stir at room temperature for 30 min. The Schlenk bomb was removed from the glovebox and heated in a preheated oil bath at 110 °C until full consumption of starting materials was achieved (24 h).

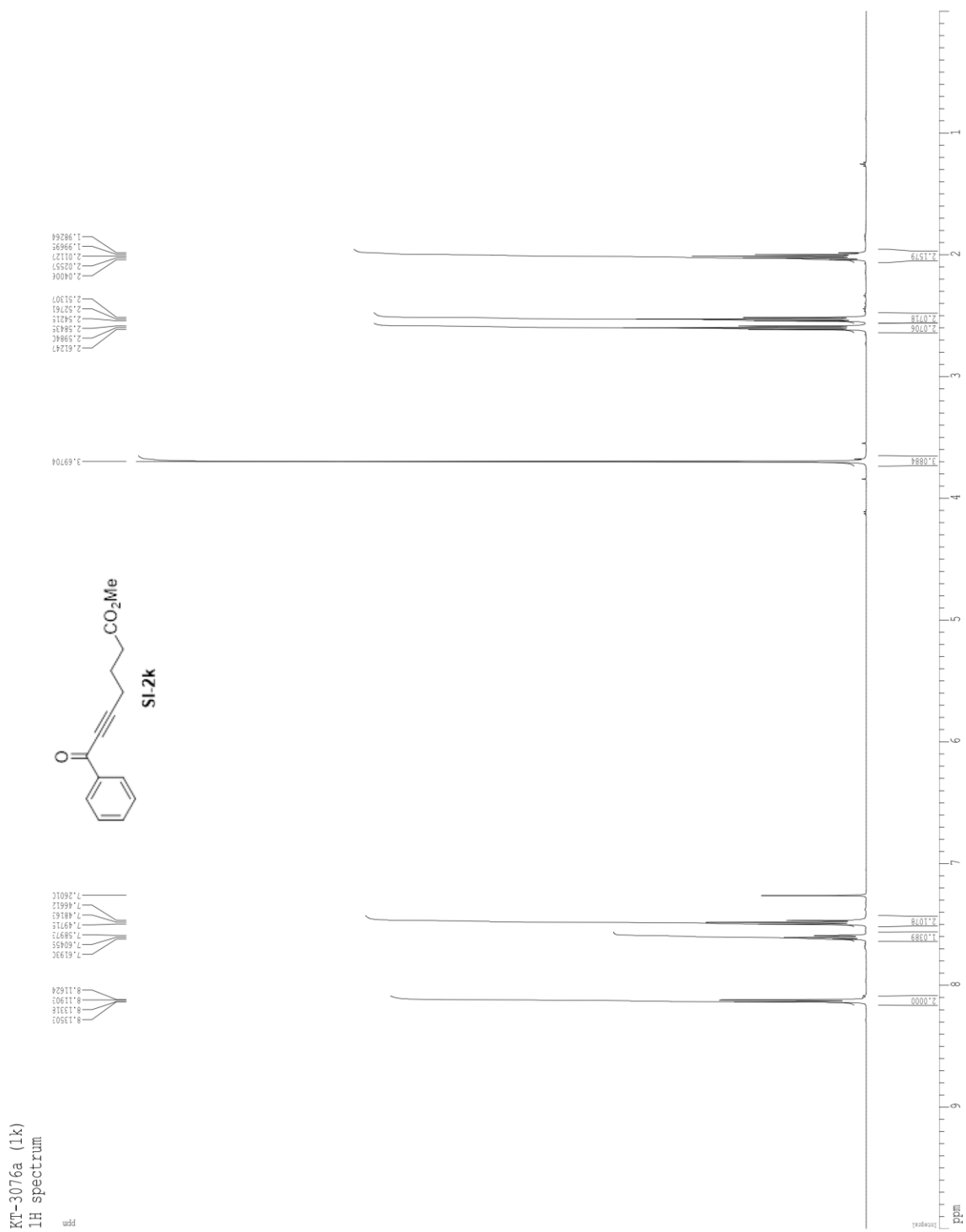
Pinacol (2.59 g, 21.9 mmol, 3.00 equiv) was dissolved in anhydrous Et<sub>3</sub>N (3.05 mL, 21.9 mmol, 3.00 equiv). The resulting solution was added to the above reaction mixture, and the resulting suspension was stirred at 25 °C for 1 h. Volatiles were removed in vacuo. The resulting light brown oil was purified by silica gel chromatography using an elution gradient from 100% hexanes to

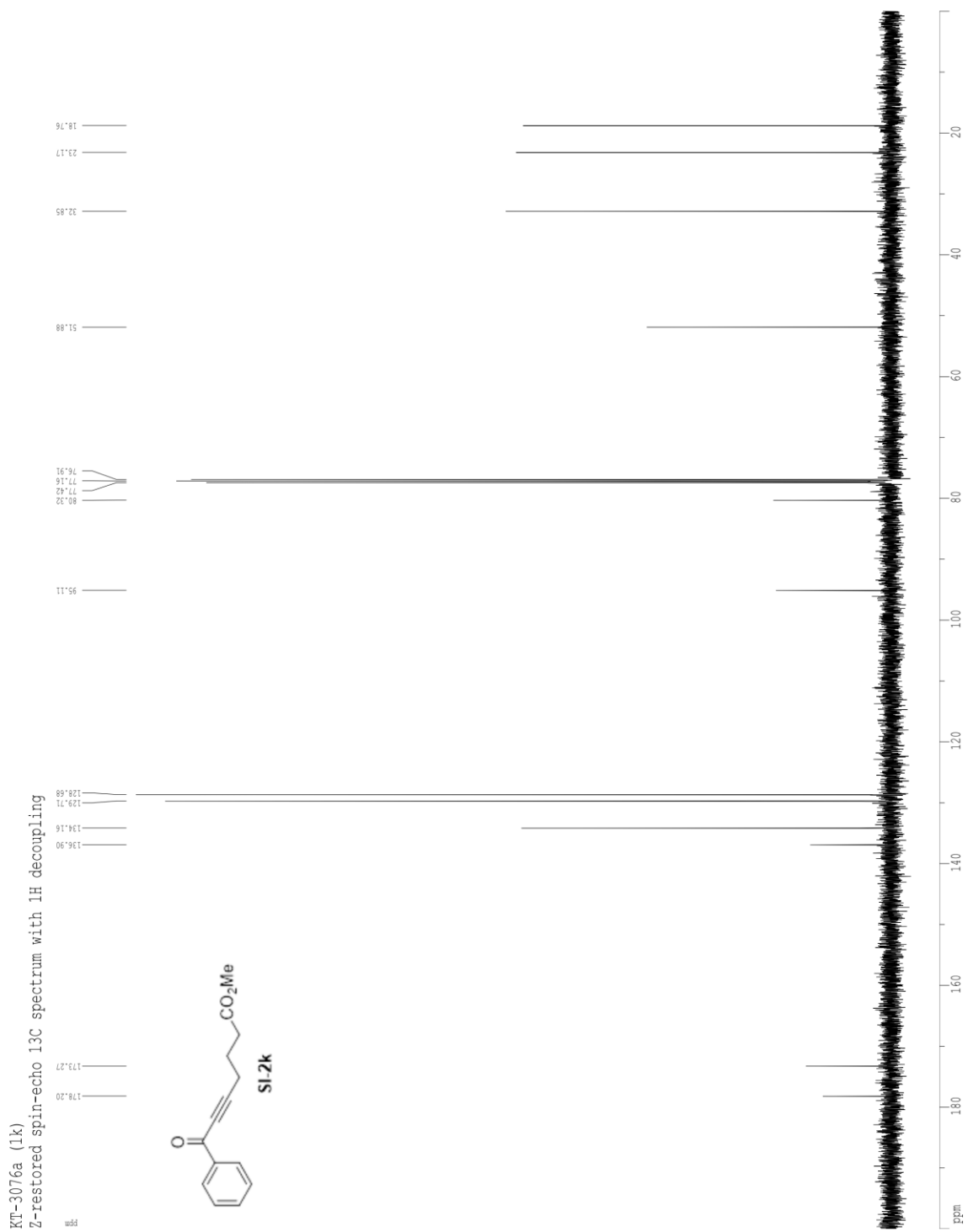
100% CH<sub>2</sub>Cl<sub>2</sub>. Solvents were removed in vacuo to afford the desired pinacol boronate **4a** as a light yellow oil (1.72 g, 72% isolated yield). Spectral data were identical to those previously obtained for this compound (see page S11).

### III. References

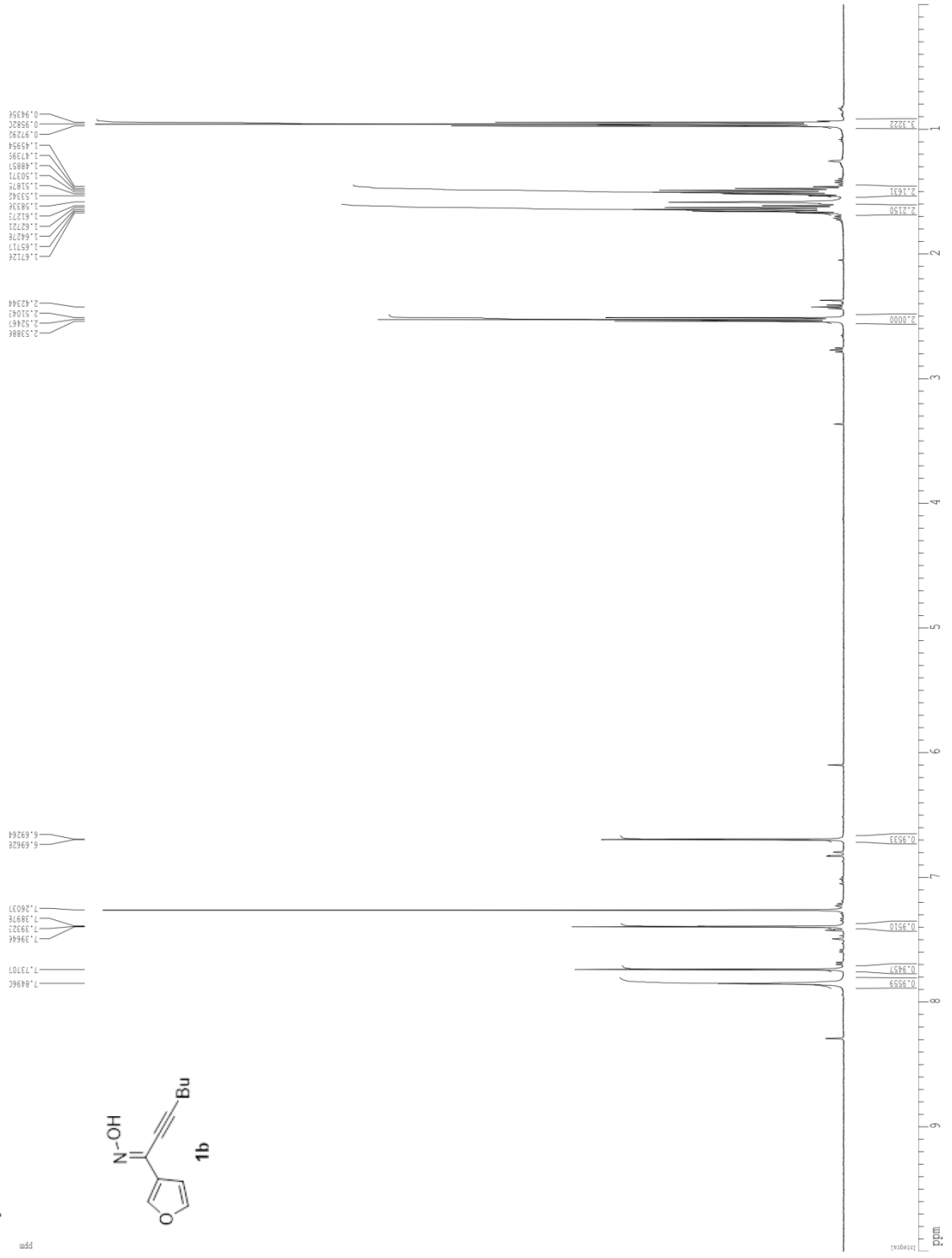
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# IV. NMR Spectra

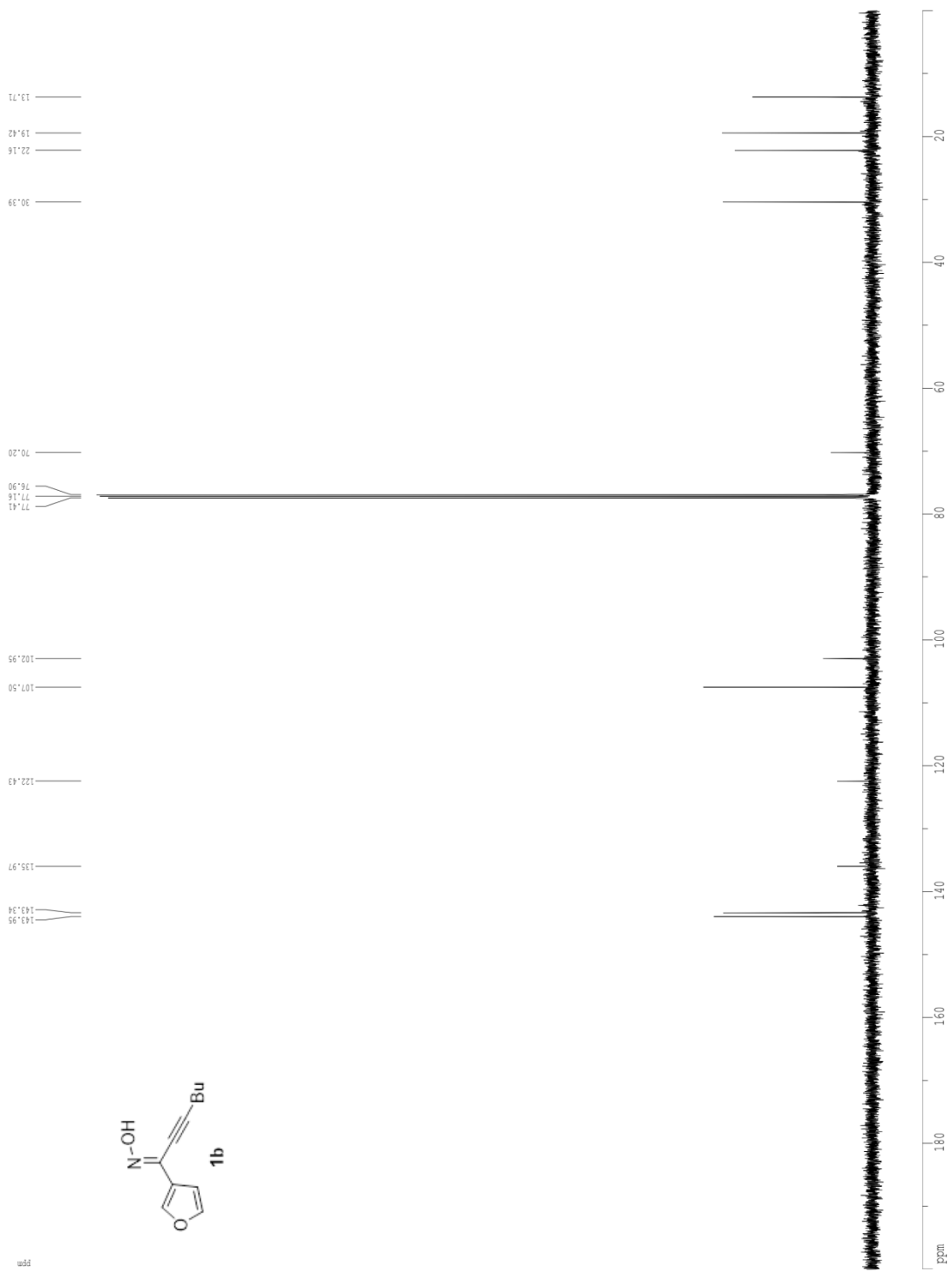




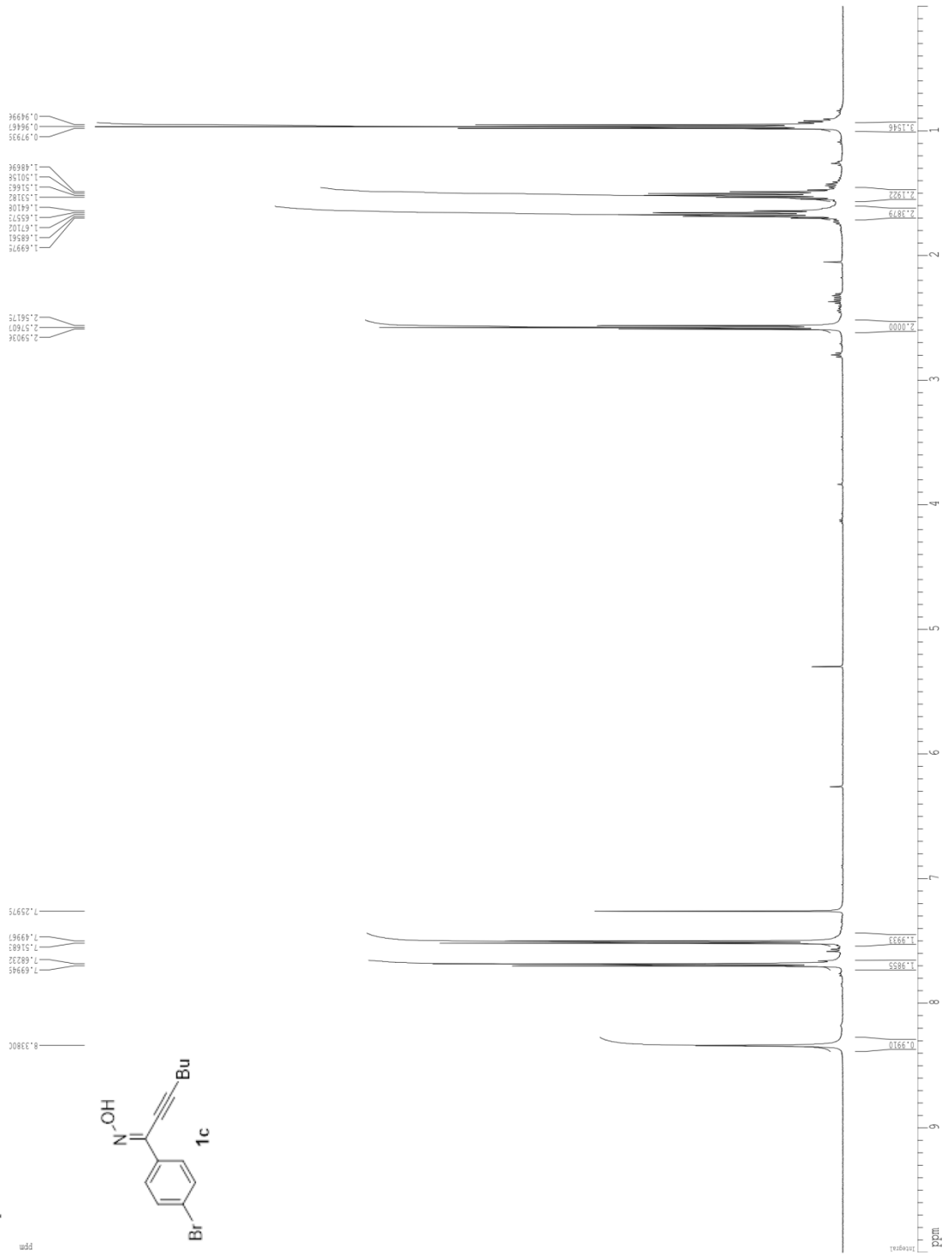
KT-II-076 (1b)  
1H spectrum



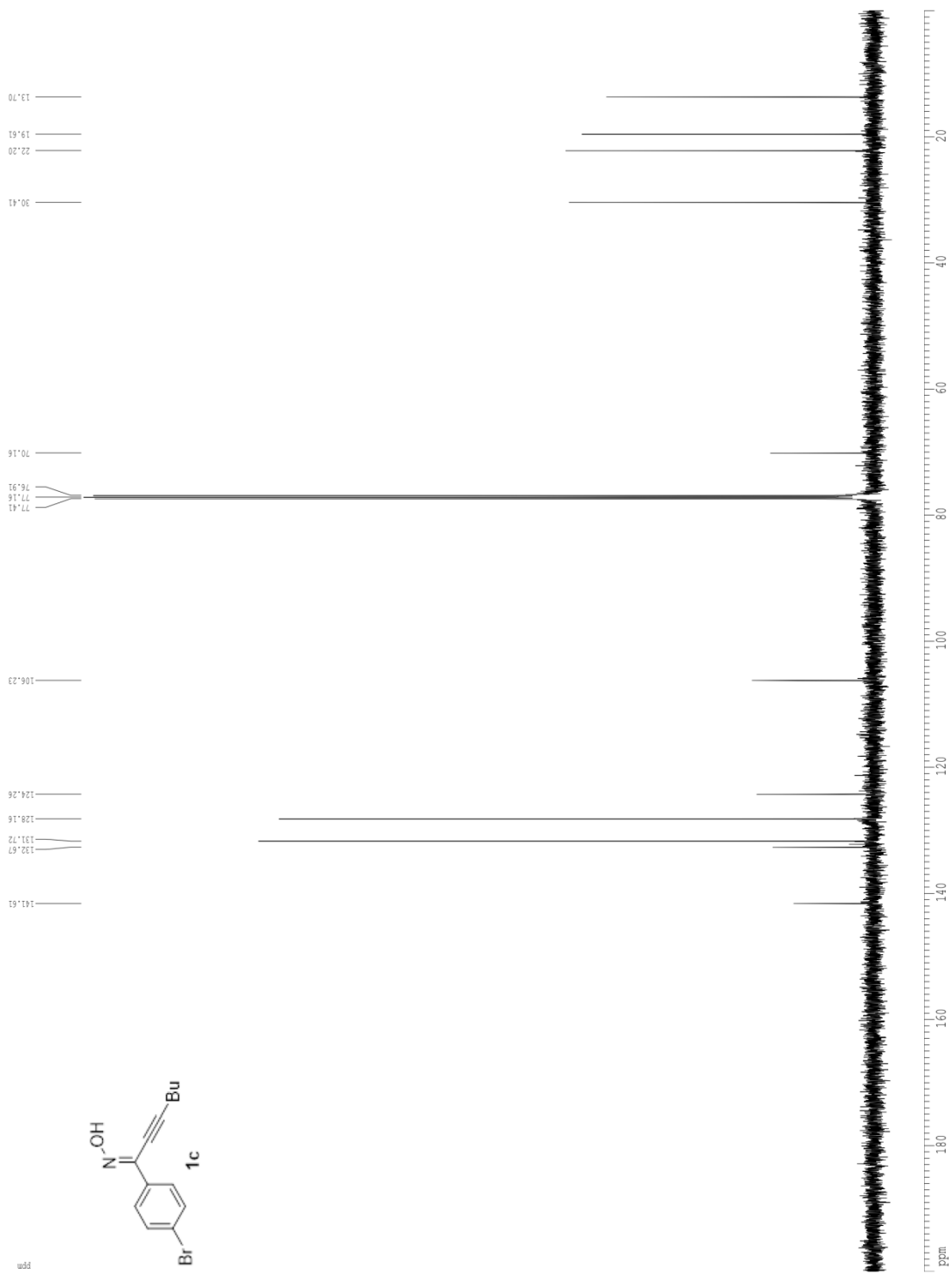
KT-II-076 (1b)  
Z-restored spin-echo 13C spectrum with 1H decoupling



KT-III-041a (1c)  
1H spectrum

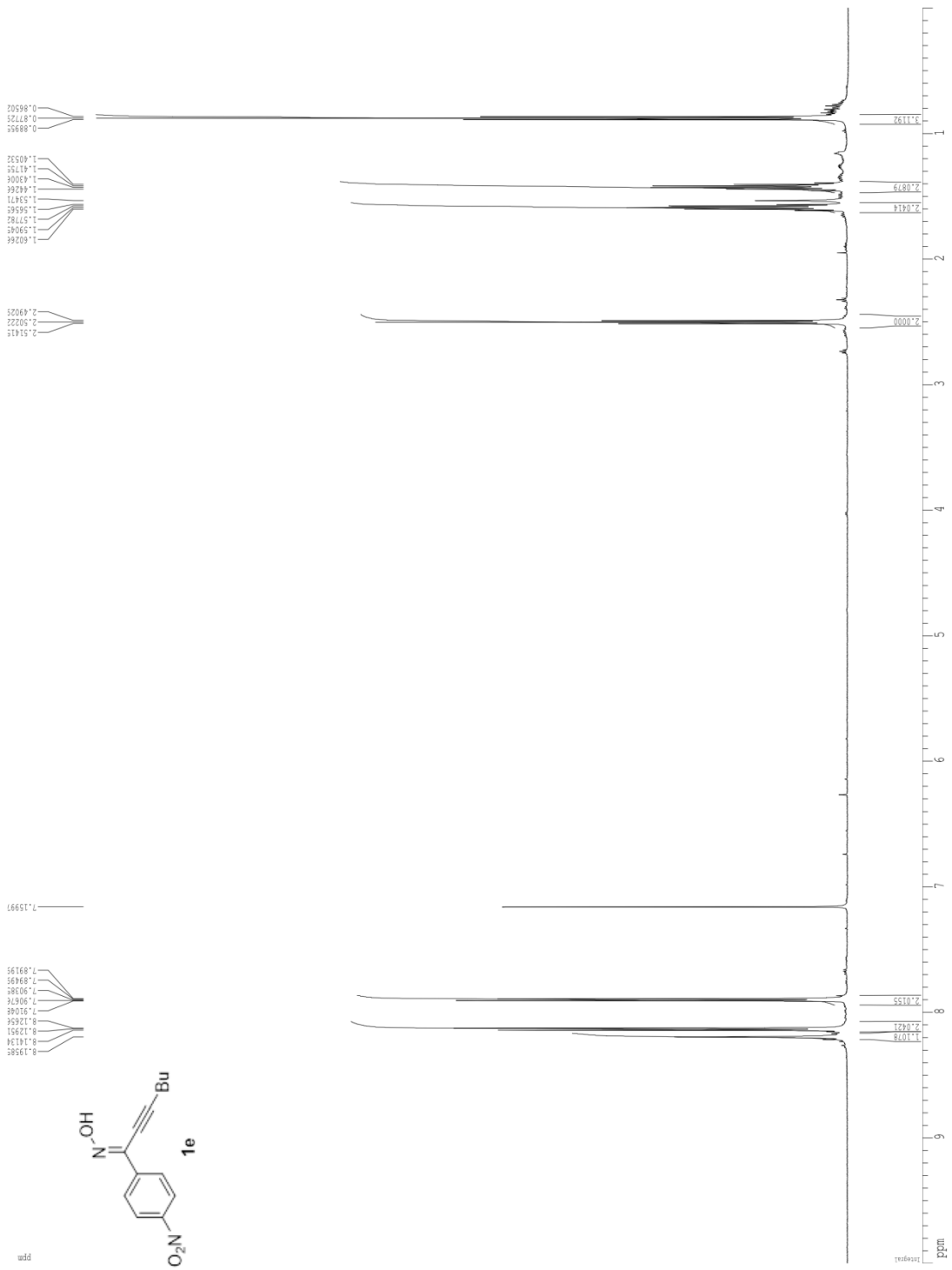
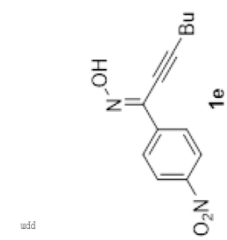


KT-III-041a (1c)  
13C spectrum with 1H decoupling

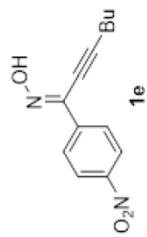
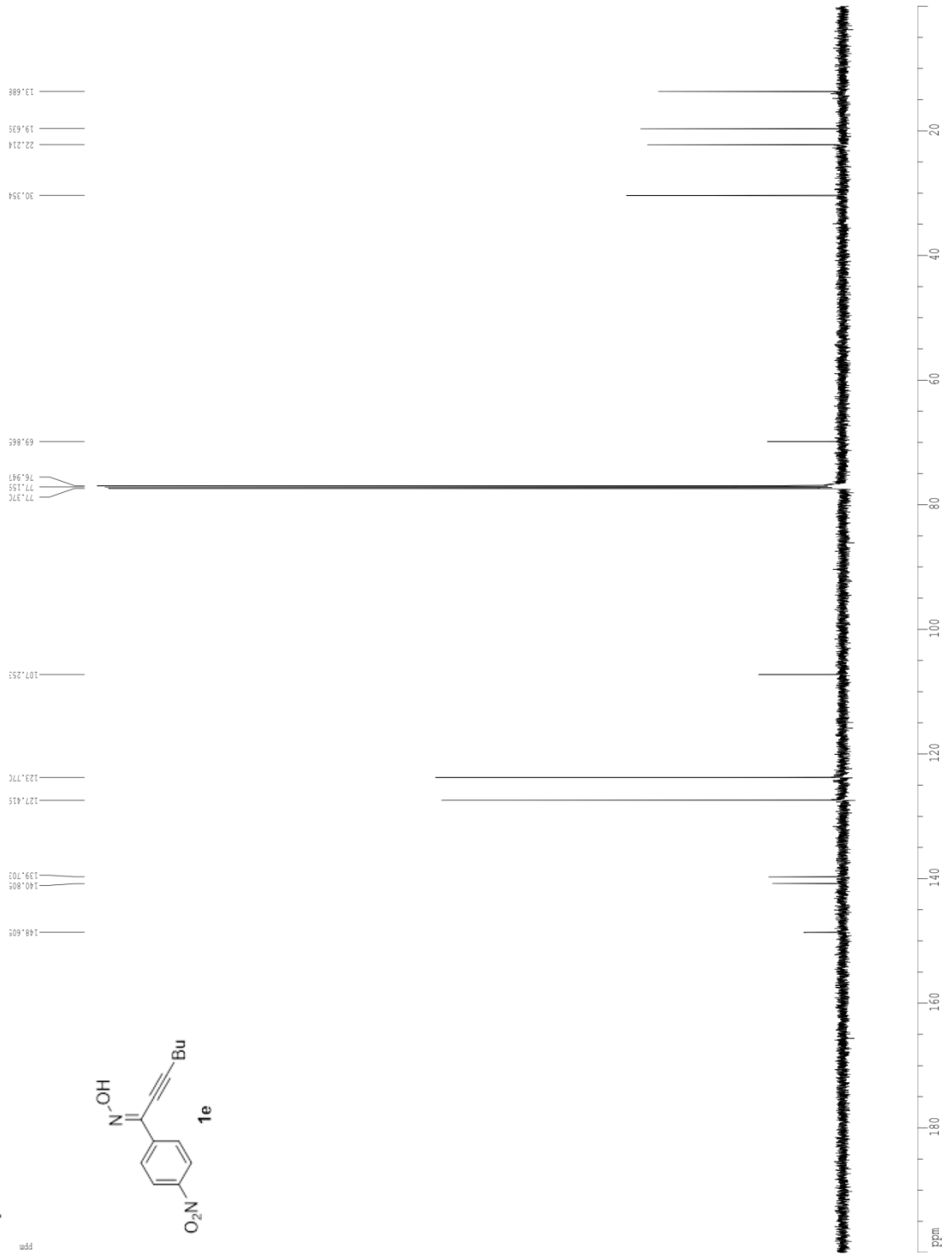




KT-III-021a (1e)  
1H spectrum

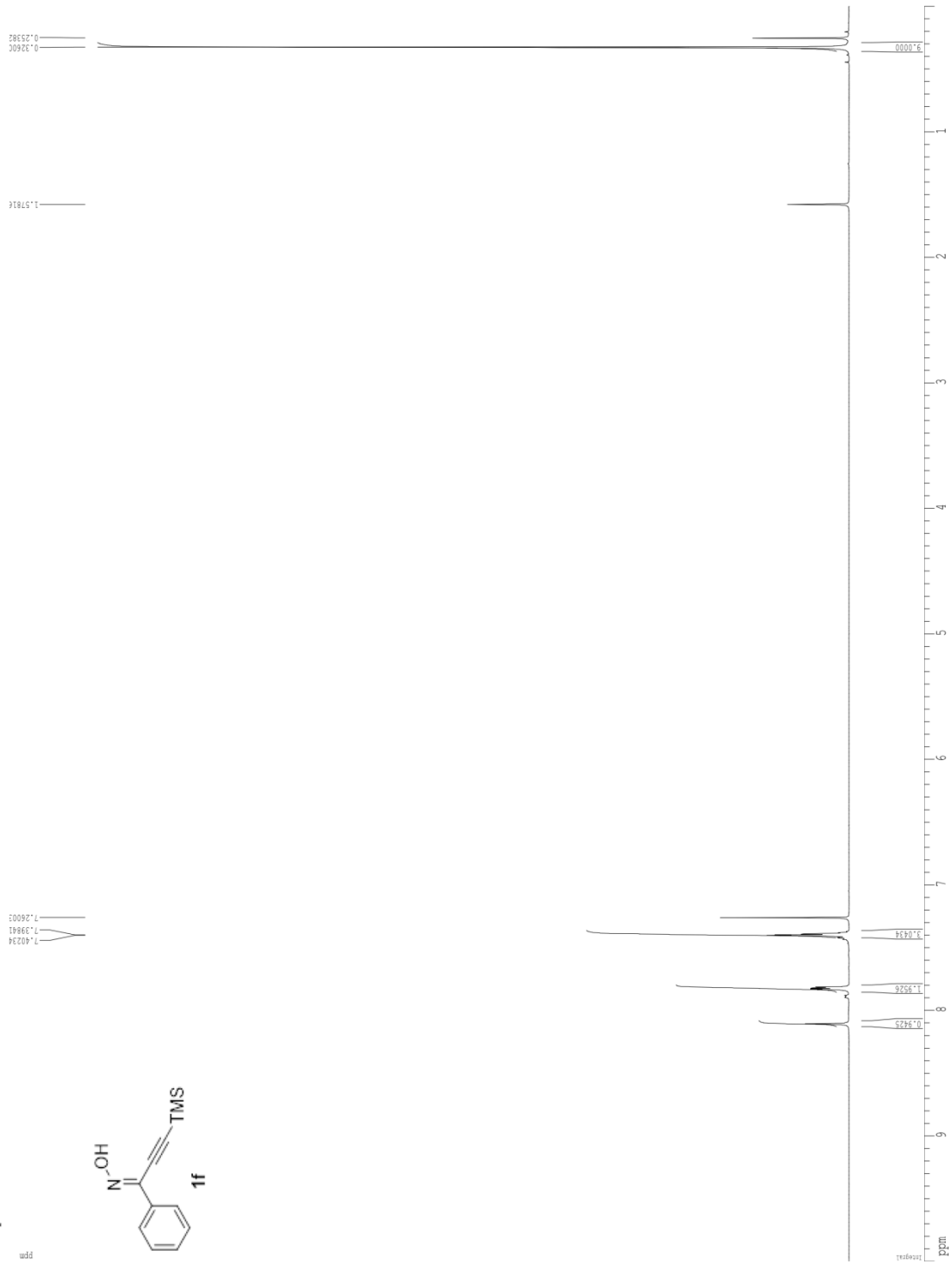
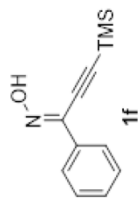


KT-III-021a (1e)  
1H spectrum

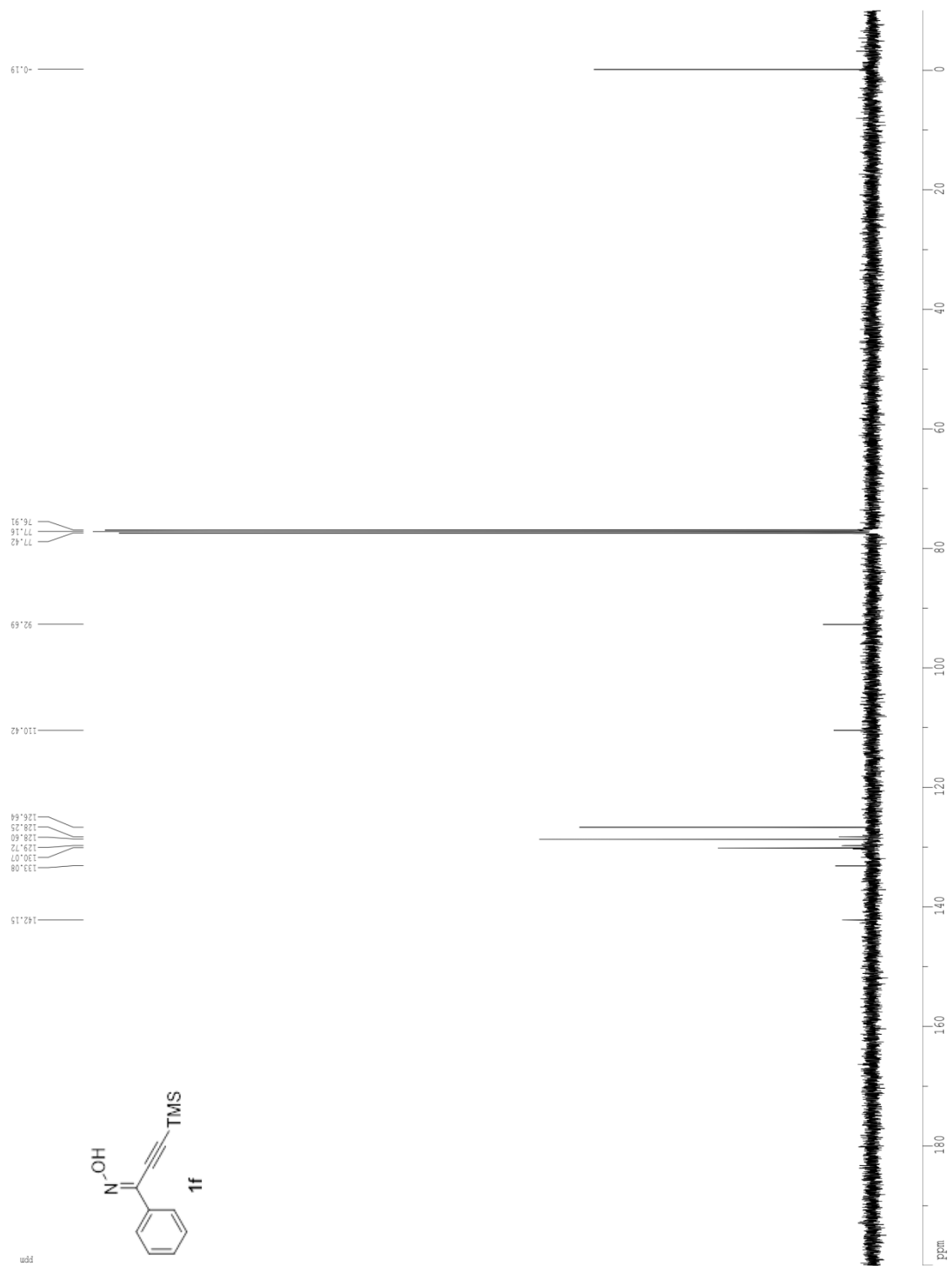


ECI-I-006 (1f)  
1H spectrum

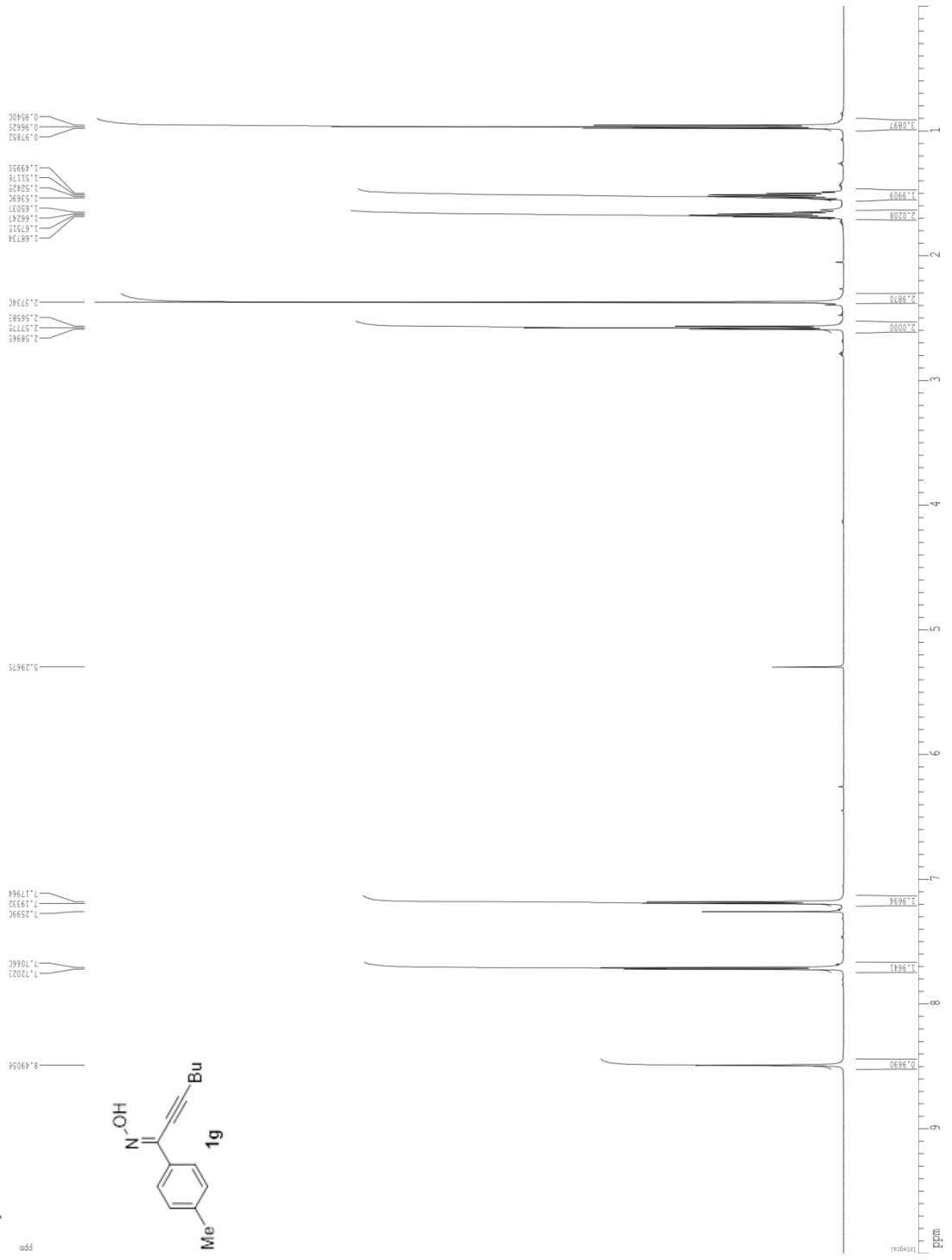
ppm



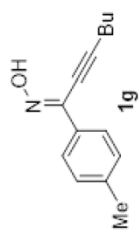
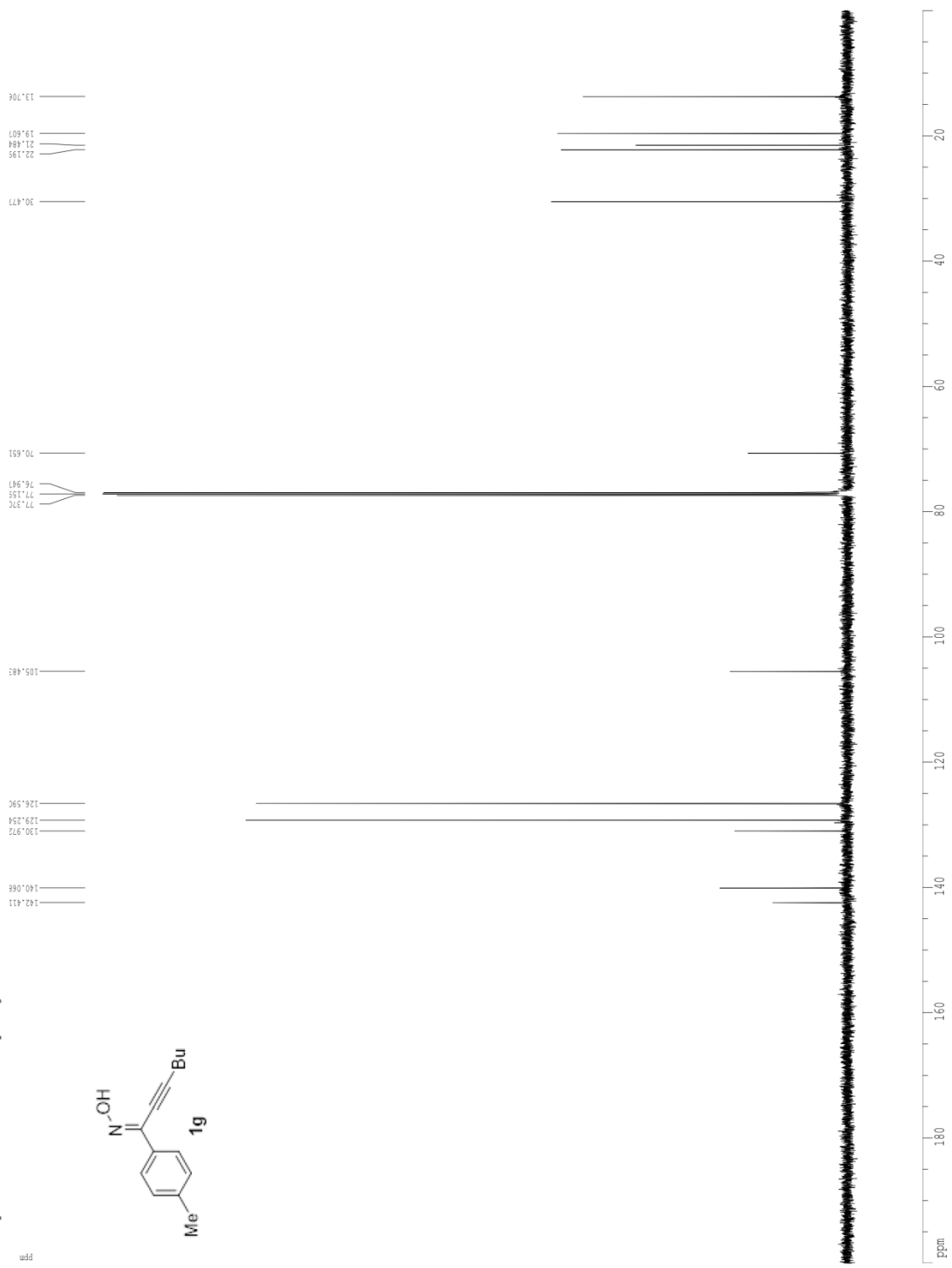
EC-I-006 (1f)  
Z-restored spin-echo 13C spectrum with 1H decoupling



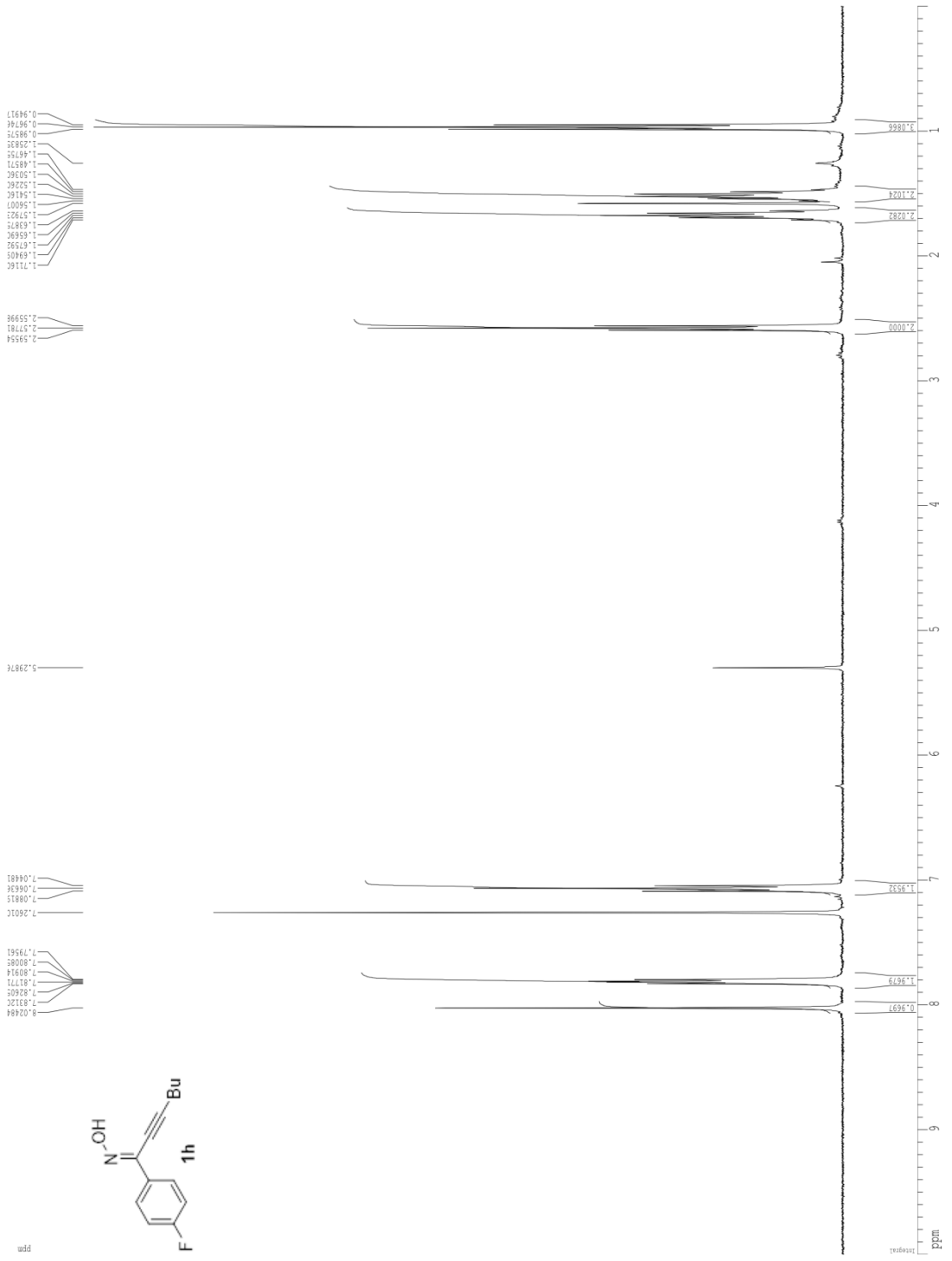
KT-III-047a (1g)  
1H spectrum

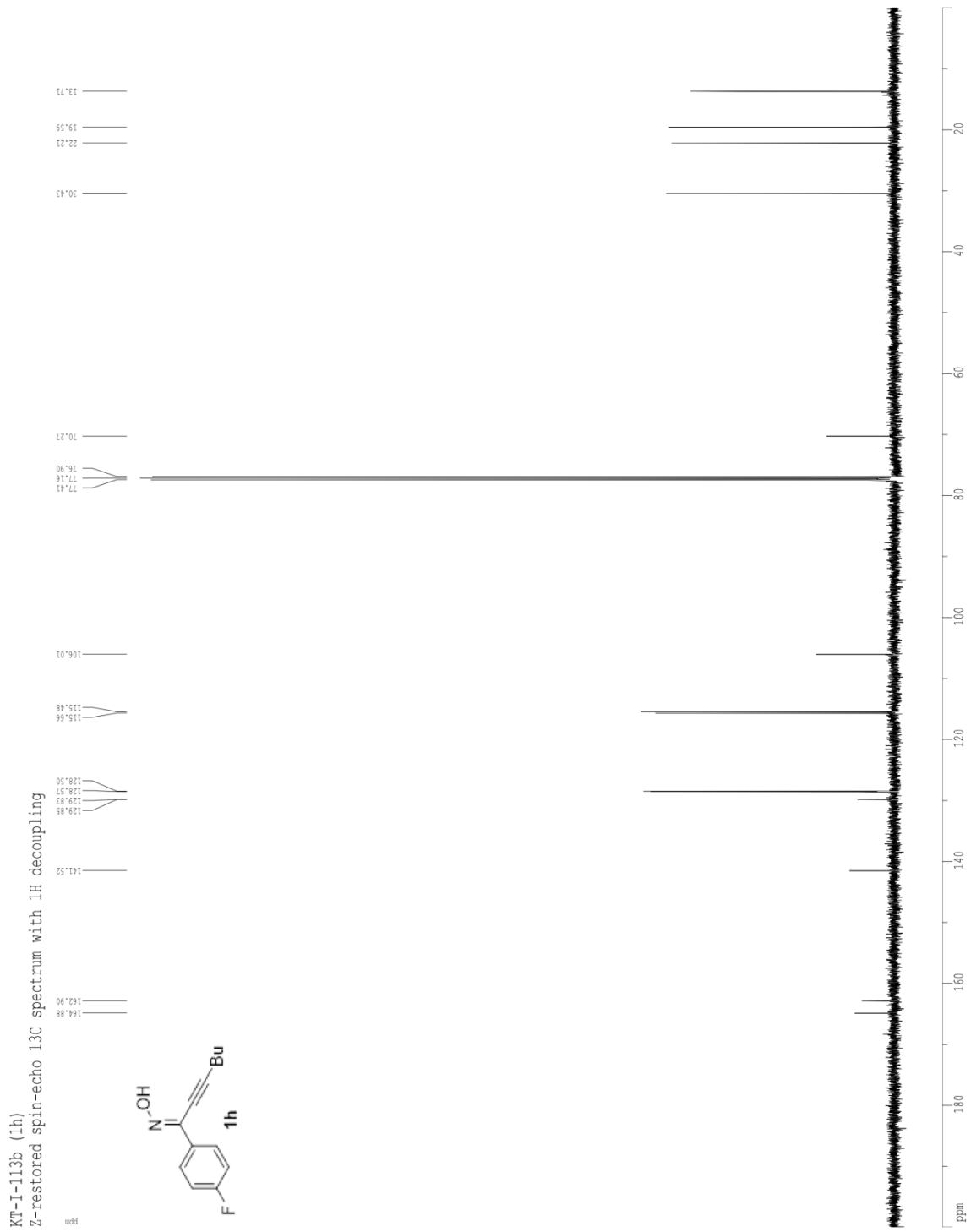


KT-III-047a (1g)  
13C spectrum with 1H decoupling



KT-I-113b (1h)  
1H spectrum

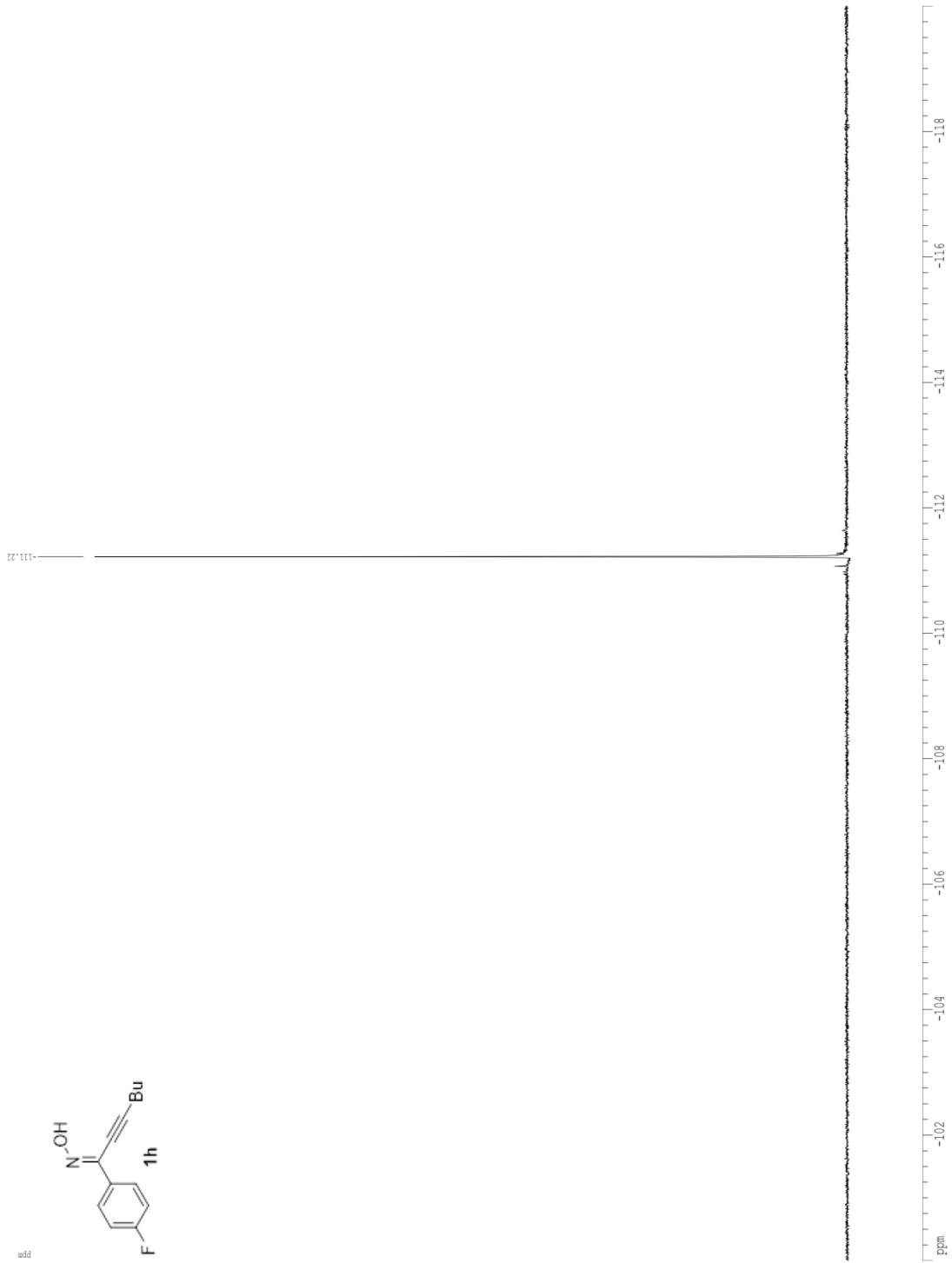
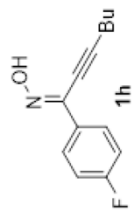






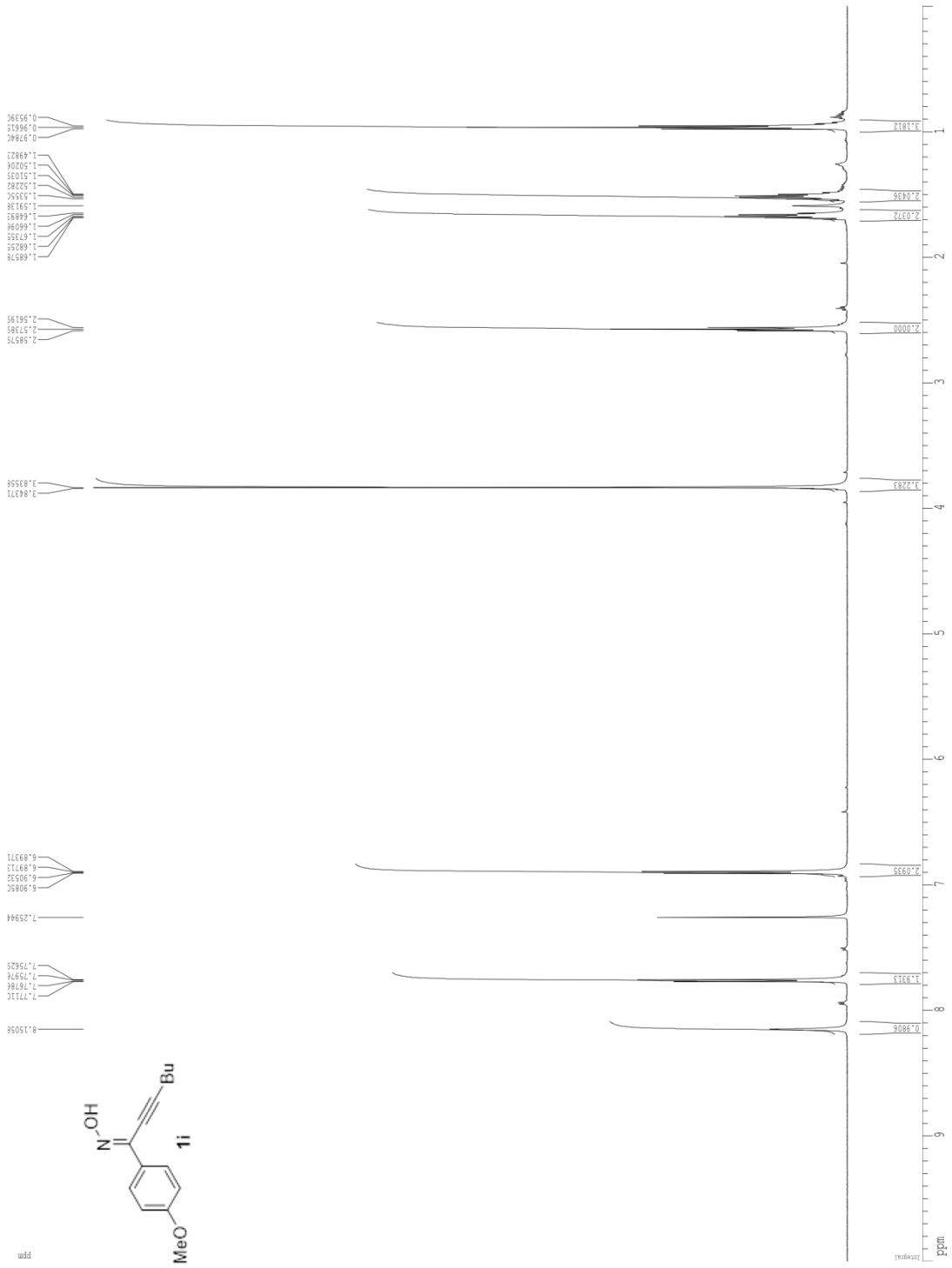
KT-I-113b (1h)  
19F spectrum with 1H decoupling

8.4

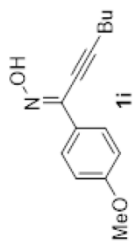
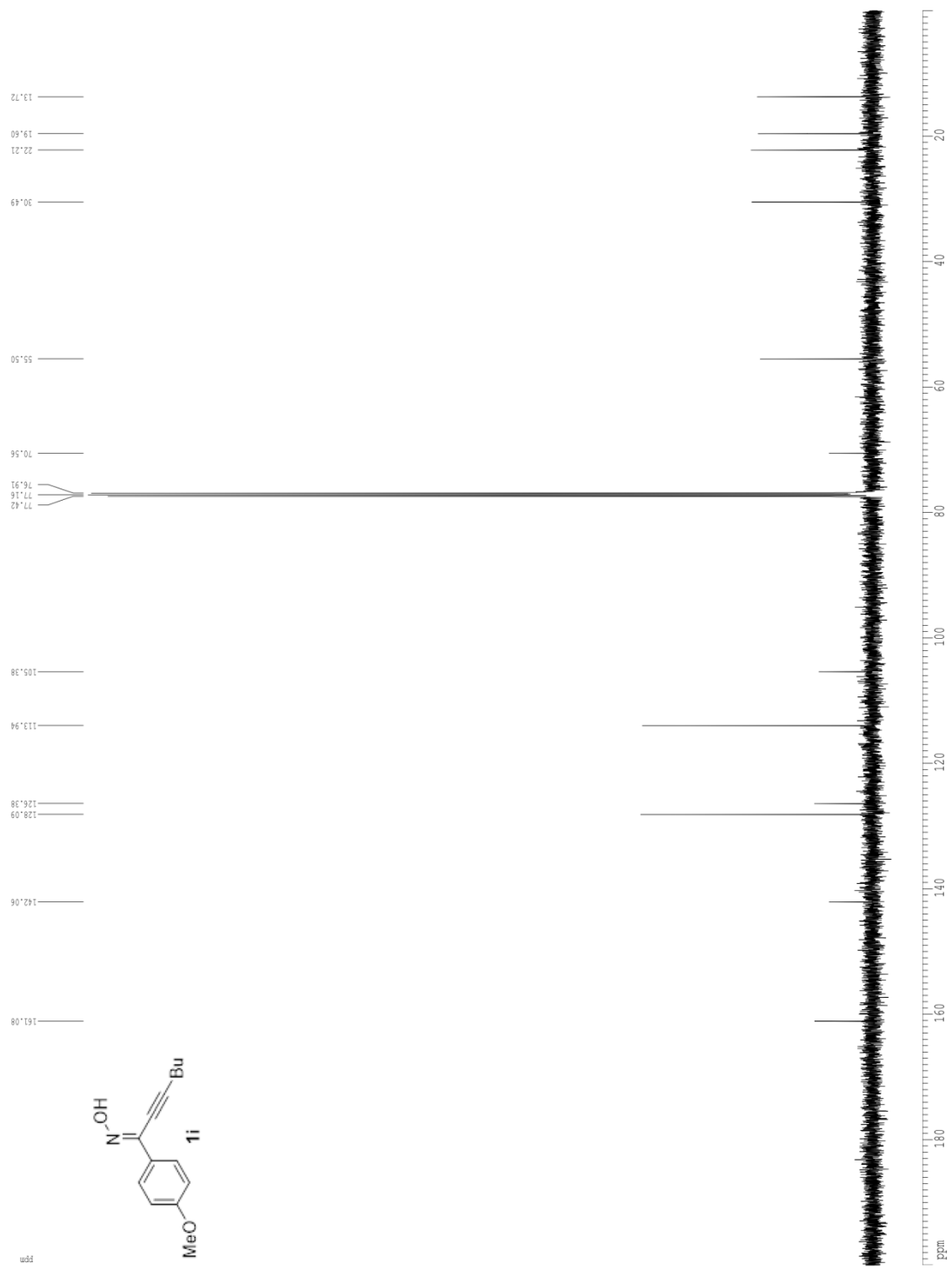


KT-III-045a (1i)  
1H spectrum

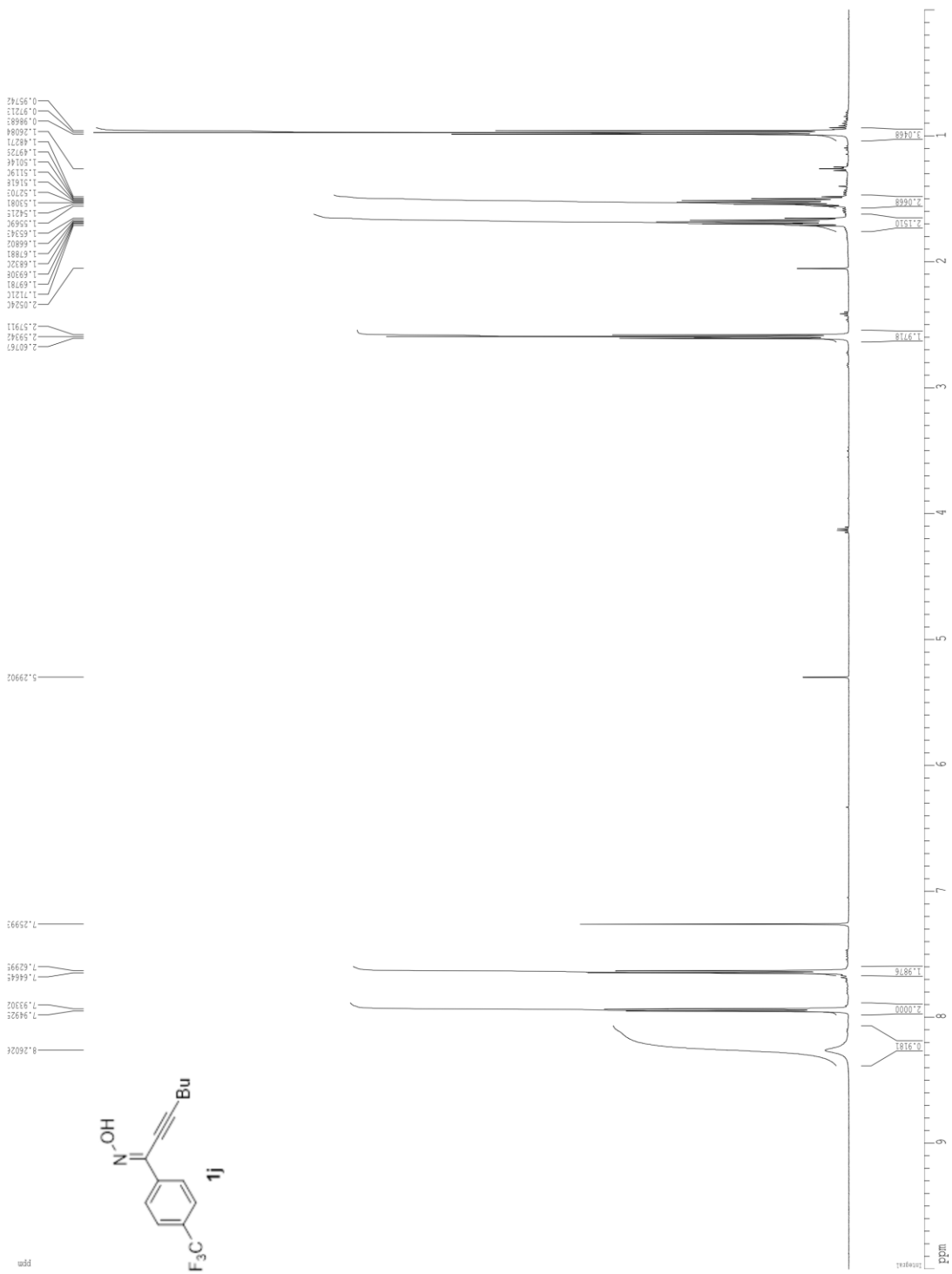
ppm



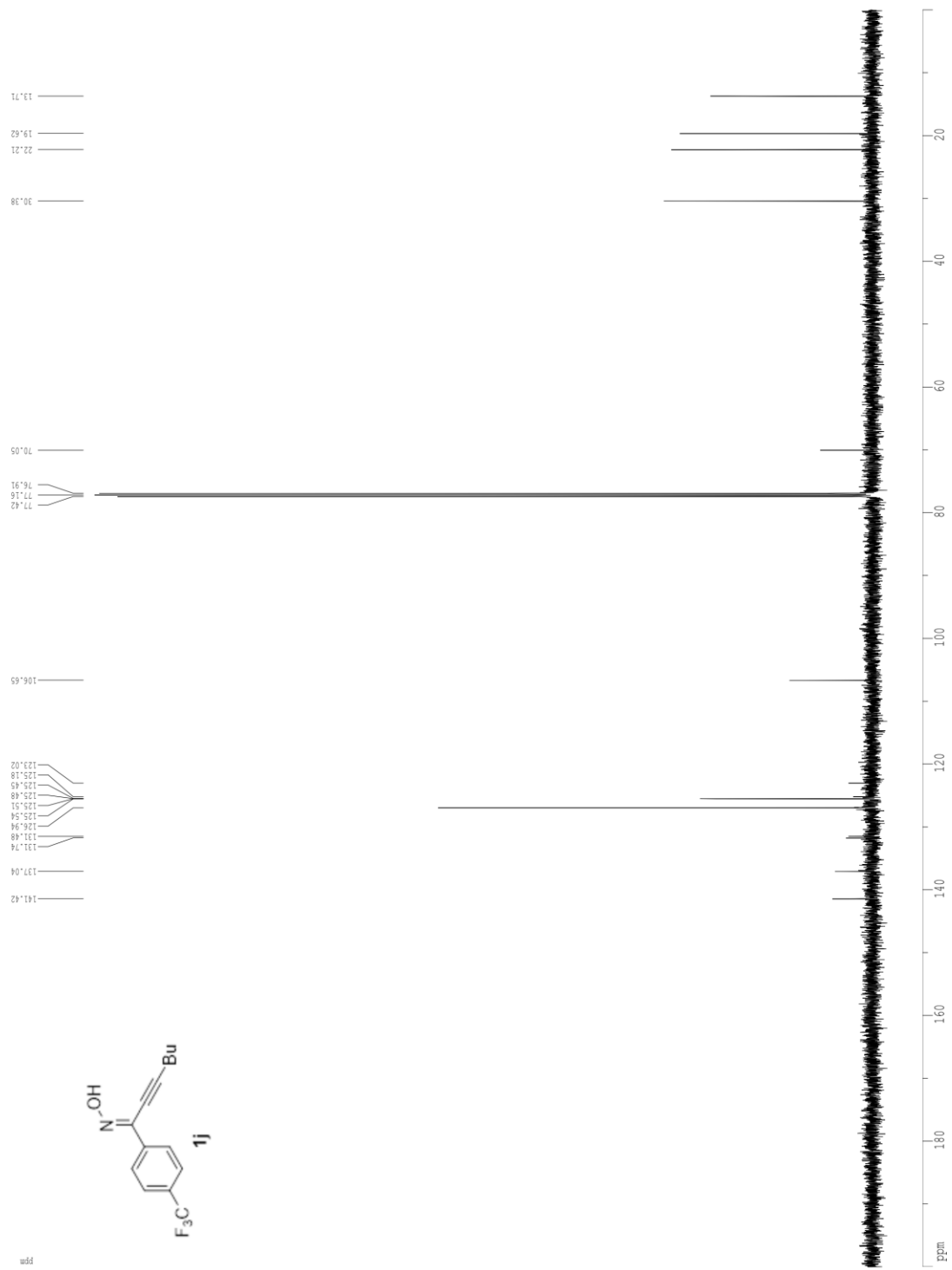
KT-III-045a (1i)  
13C spectrum with 1H decoupling



KT-3068a (1j)  
1H spectrum

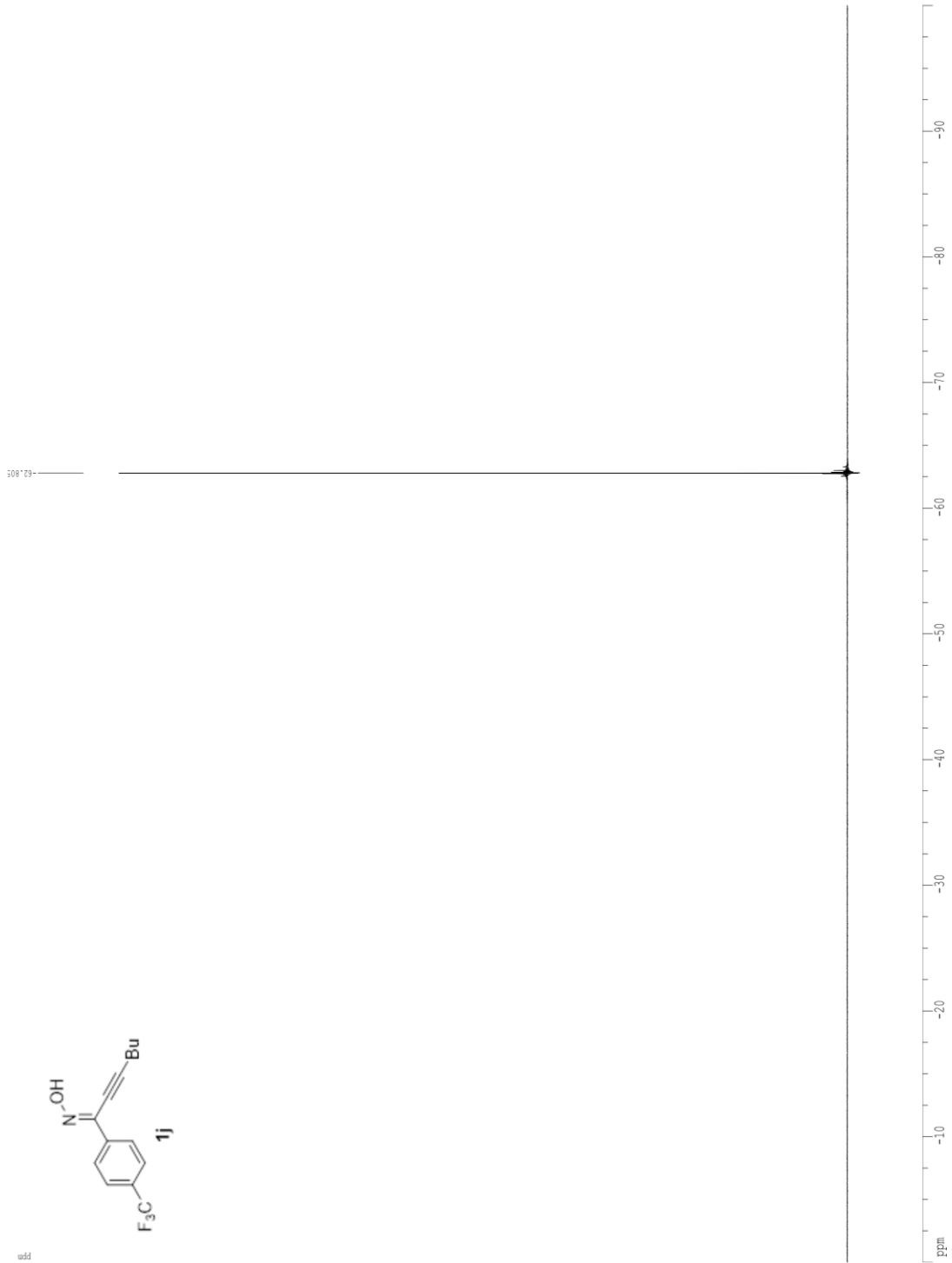
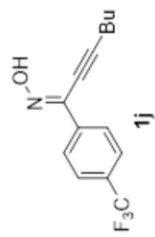


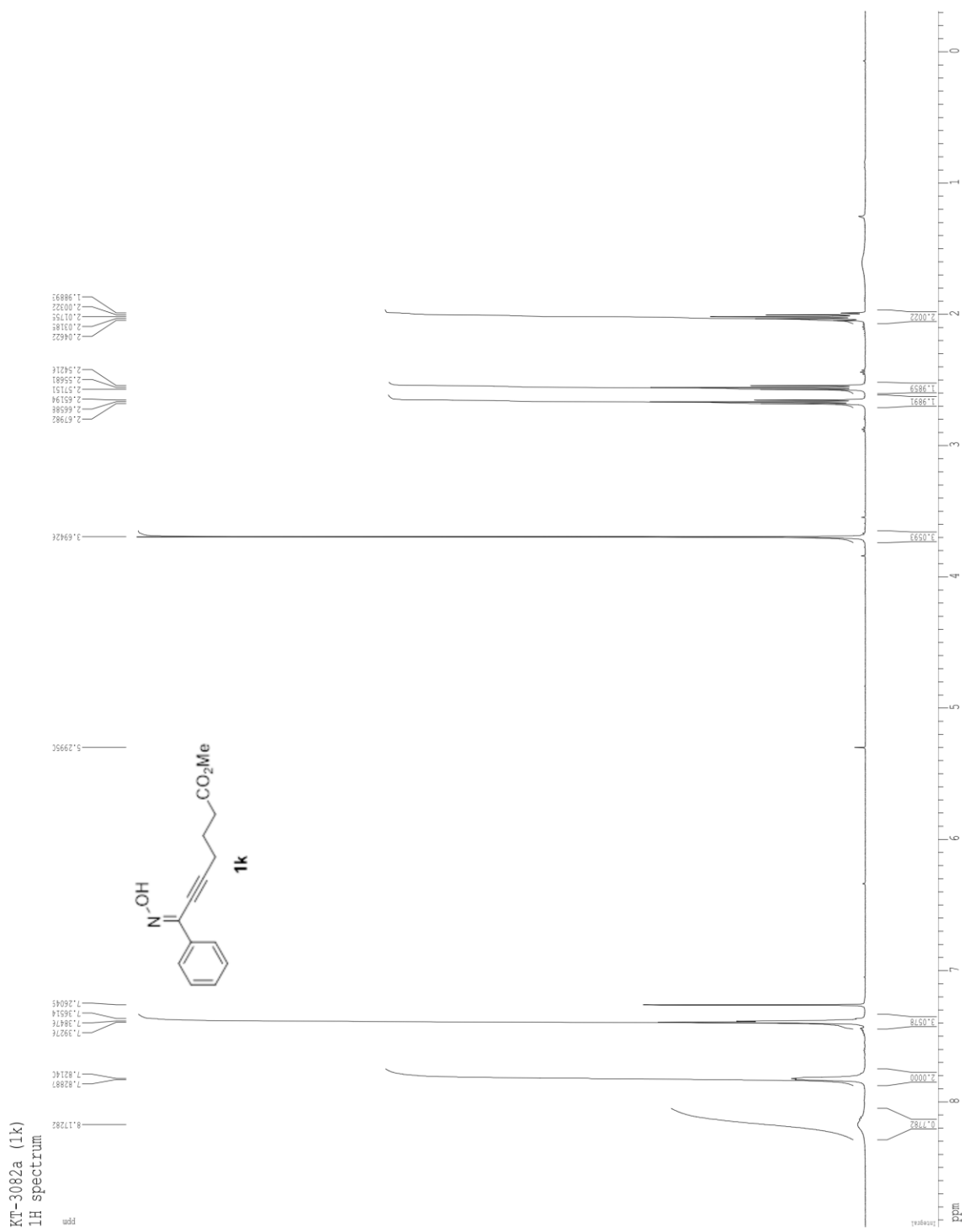
KT-3068a (1j)  
Z-restored spin-echo 13C spectrum with 1H decoupling

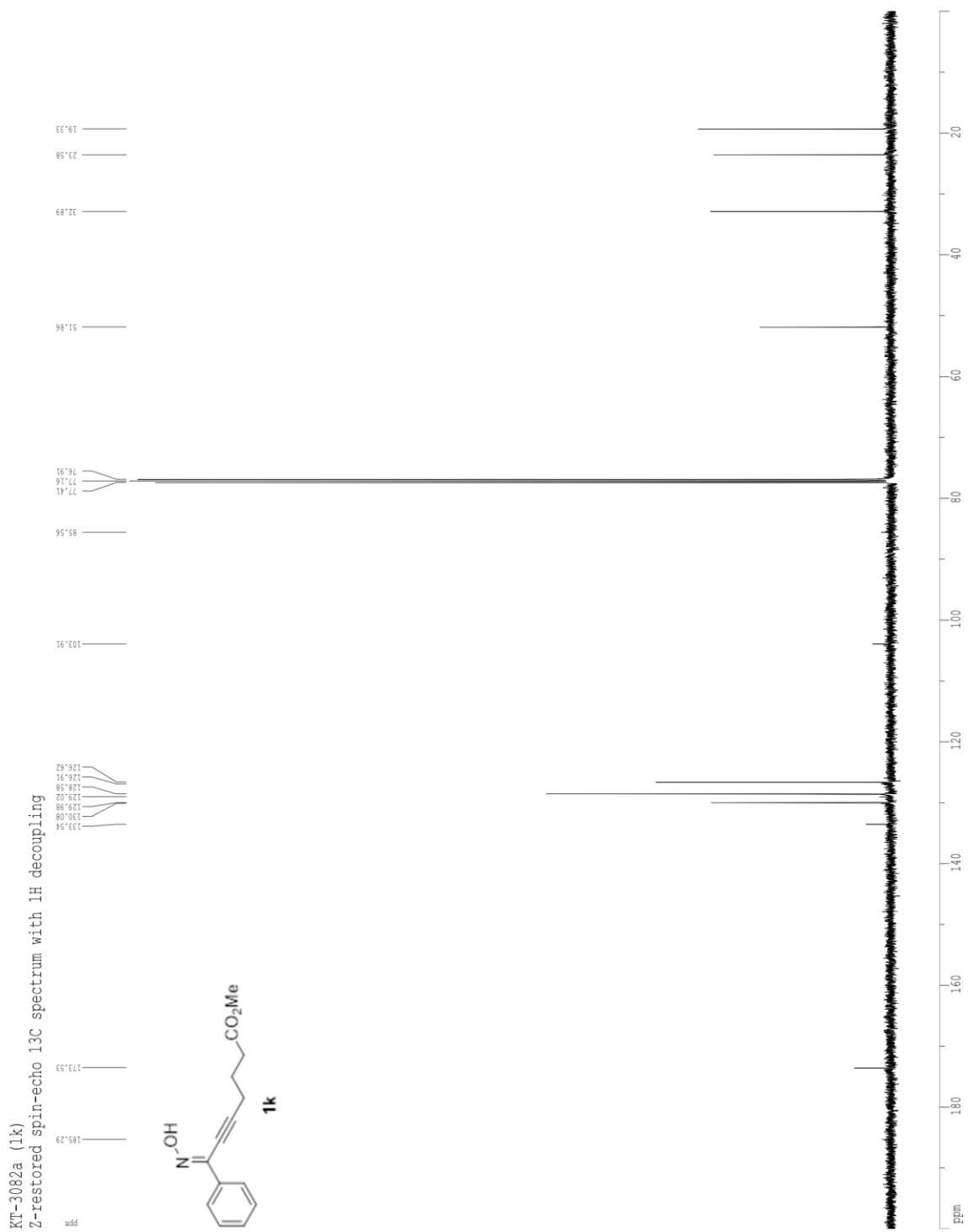


KT-3068a (1j)  
19F spectrum with 1H decoupling

100

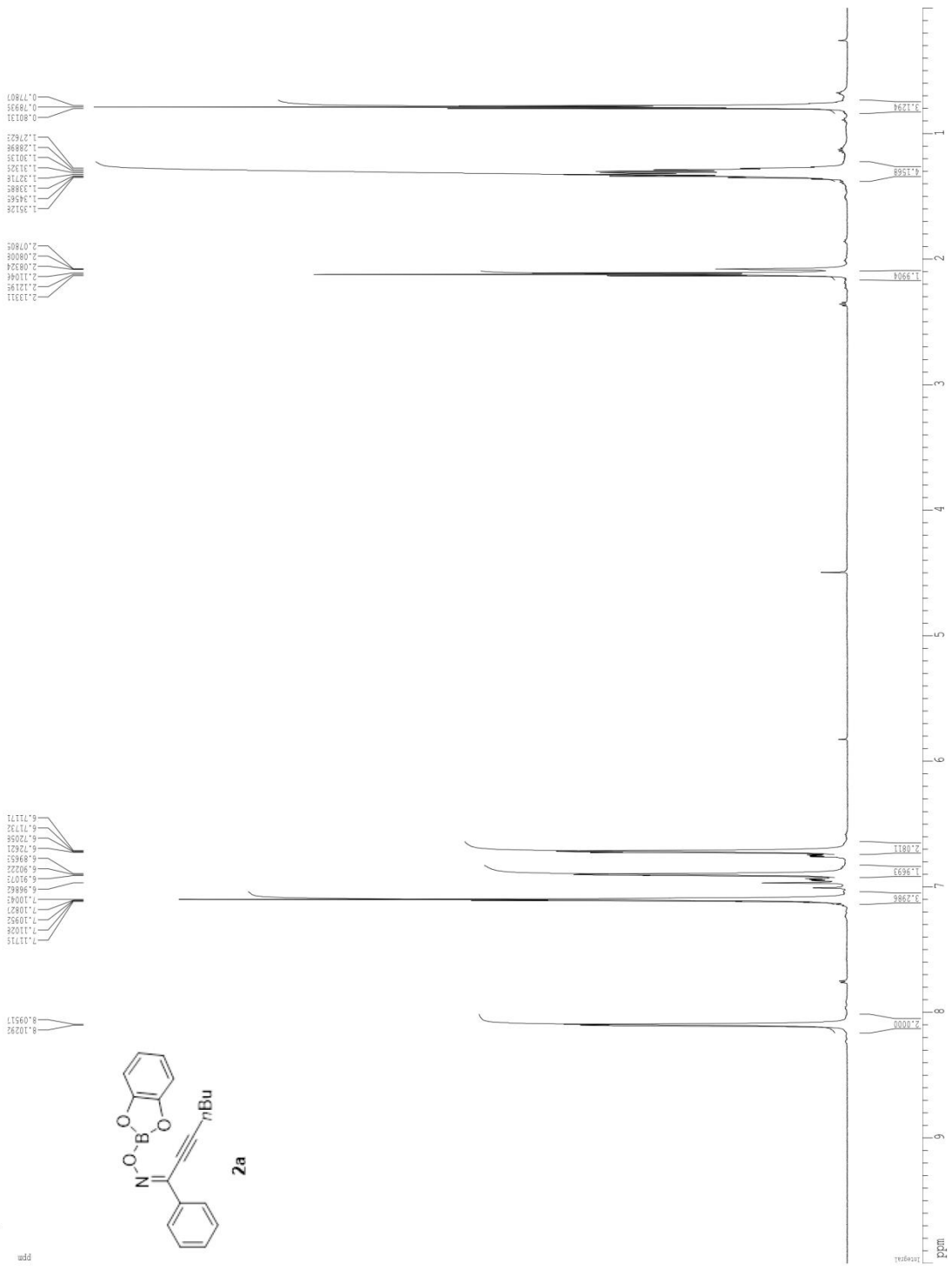




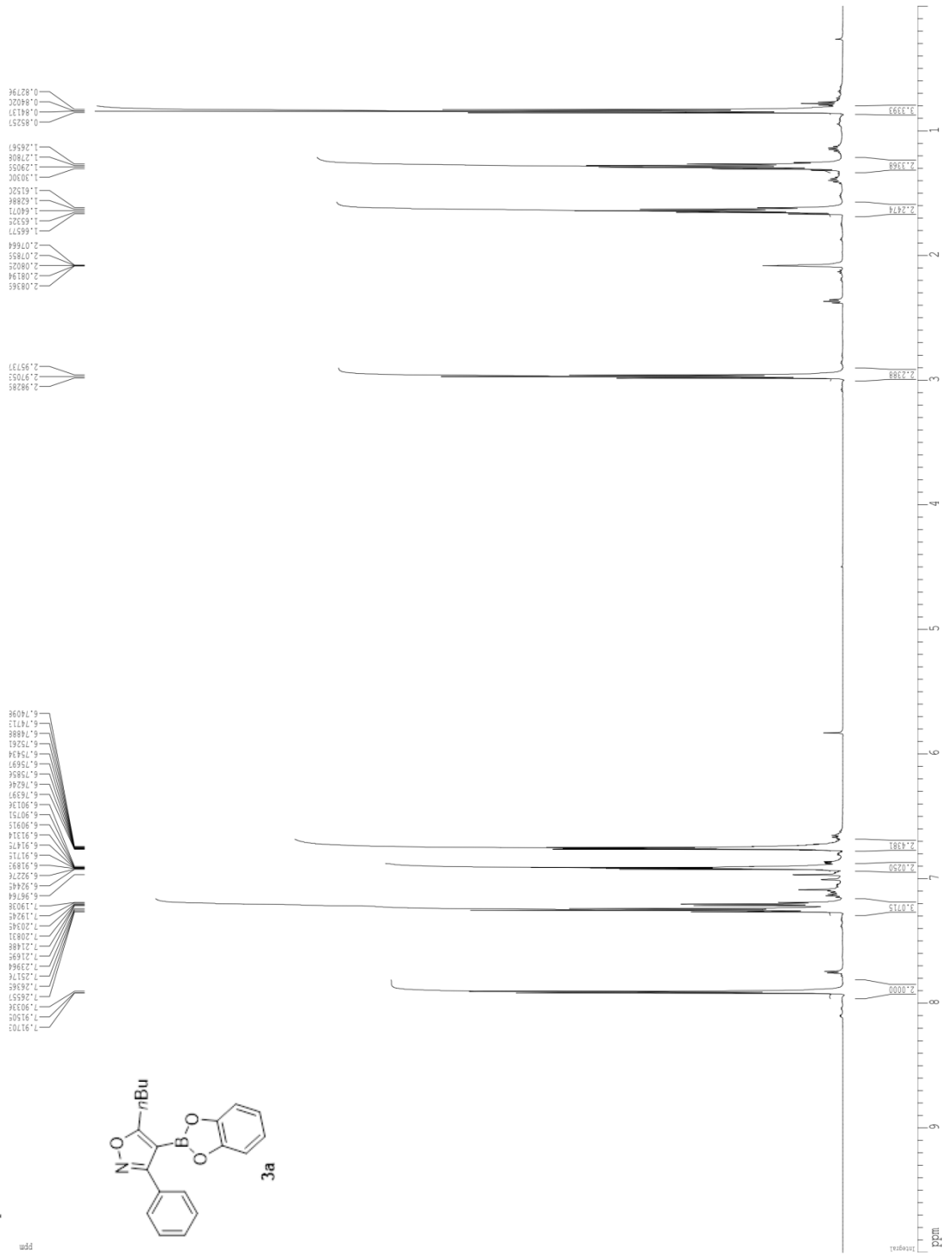




KT-III-044a (2a)  
1H spectrum

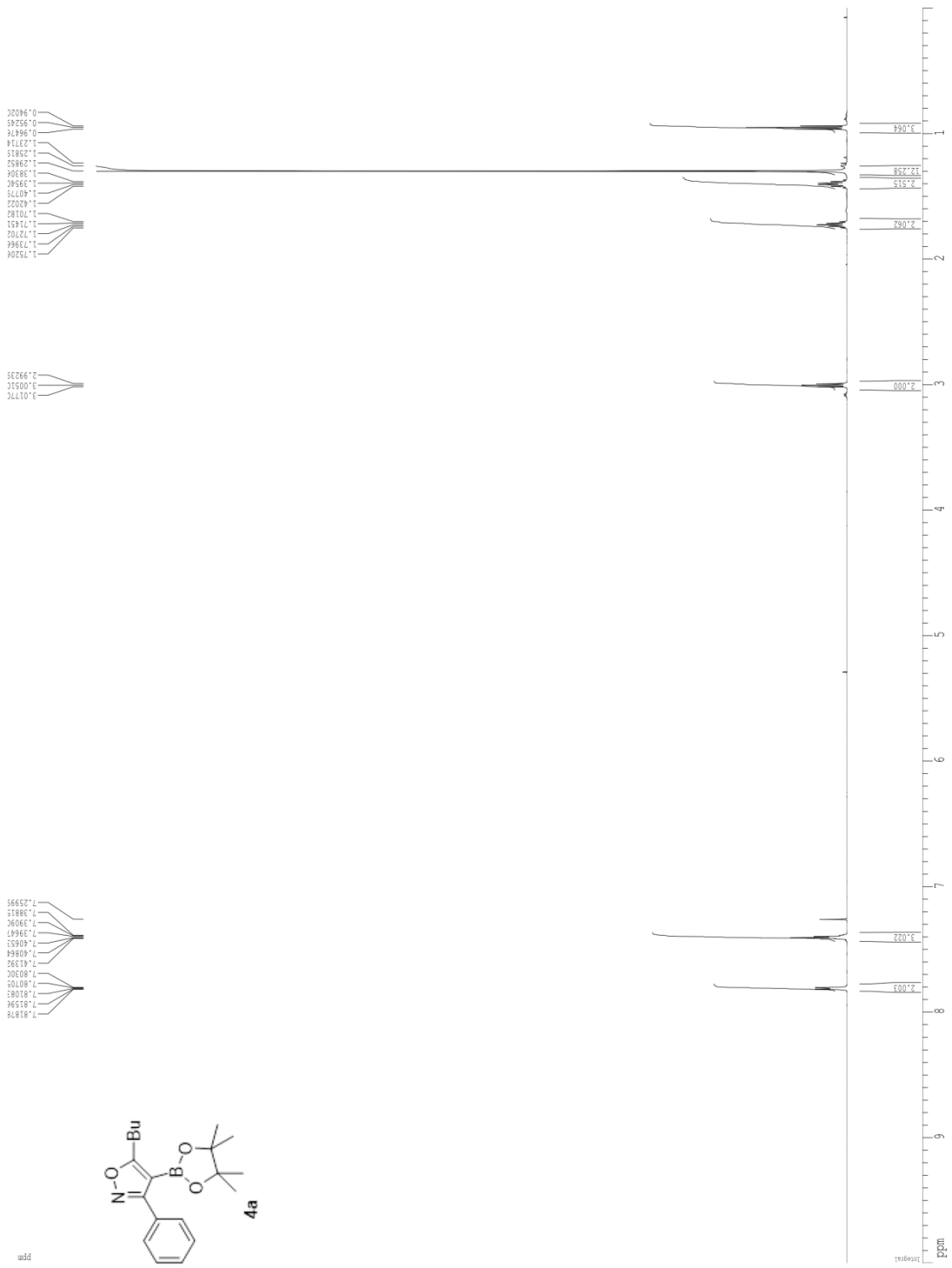


KT-III-044e (3a)  
<sup>1</sup>H spectrum

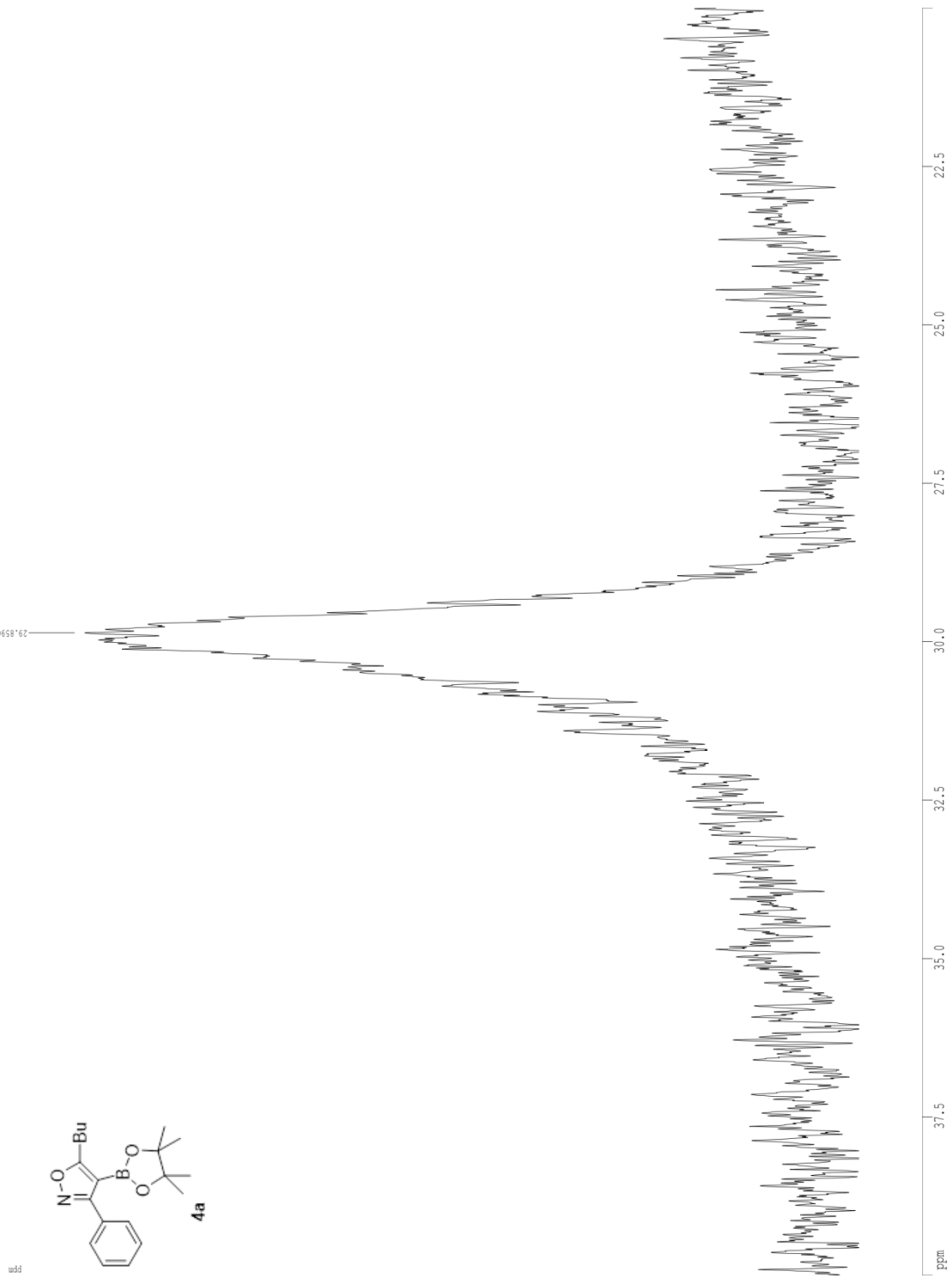


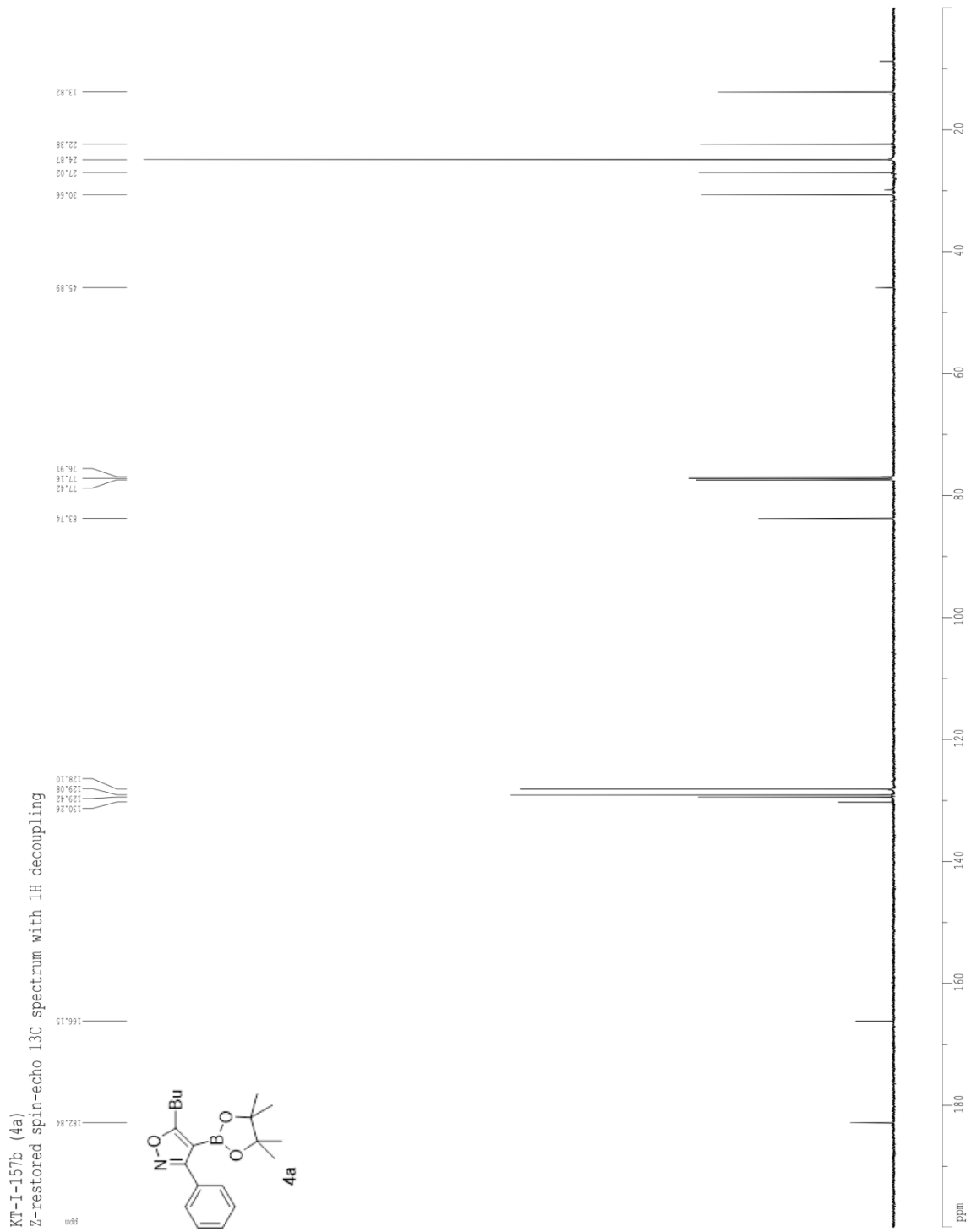
KT-I-157b (4a)  
1H spectrum

ppm

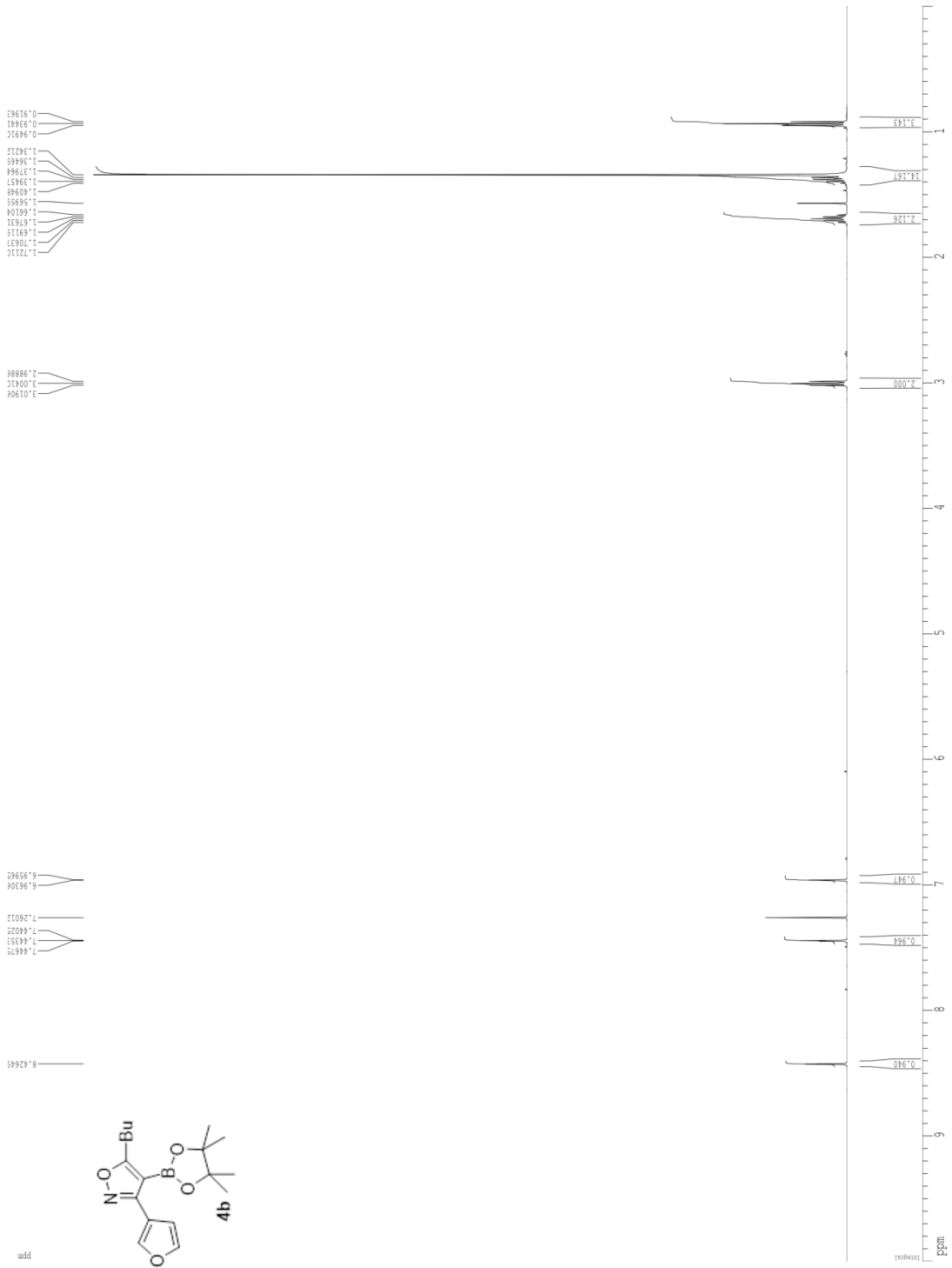


KT-I-157b (4a)  
11B spectrum using composite pulse for background suppression

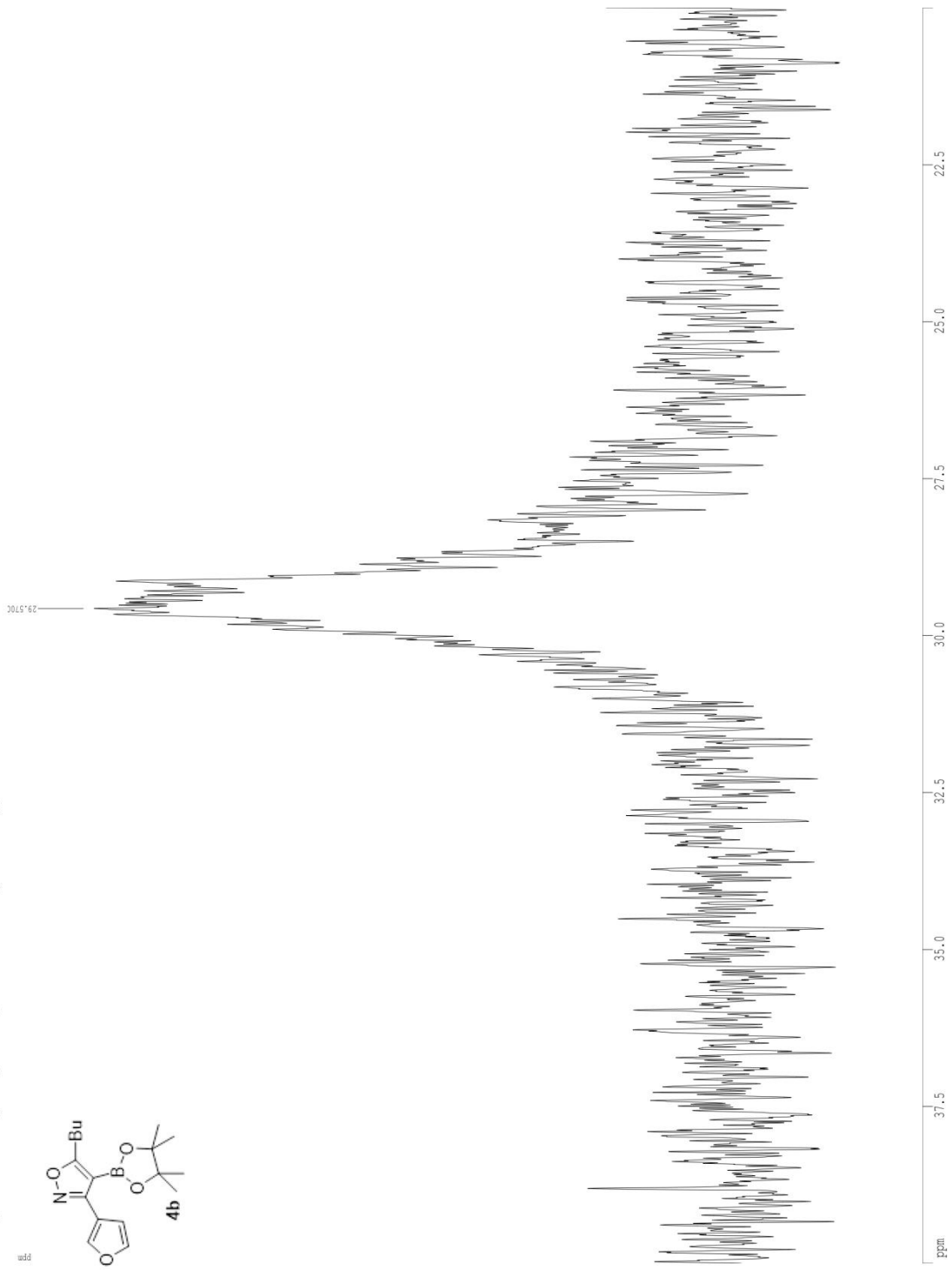




KT-II-127d (4b)  
<sup>1</sup>H spectrum



KT-II-127c (4b)  
11B spectrum using composite pulse for background suppression



KT-II-127d (4b)  
Z-restored spin-echo 13C spectrum with 1H decoupling



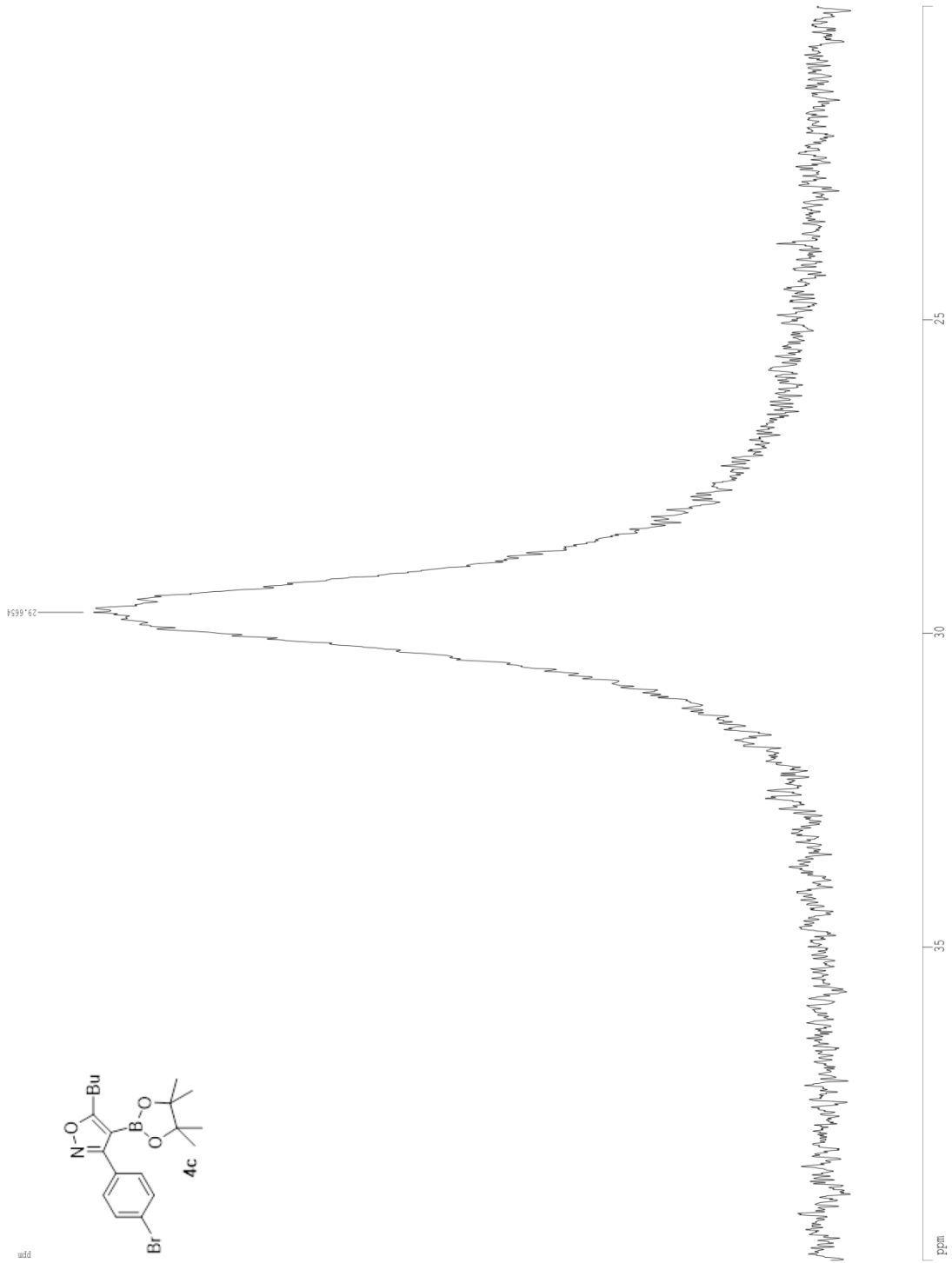
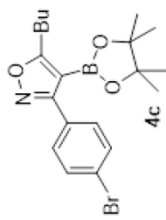


KT-II-031b (4c)  
 1H spectrum

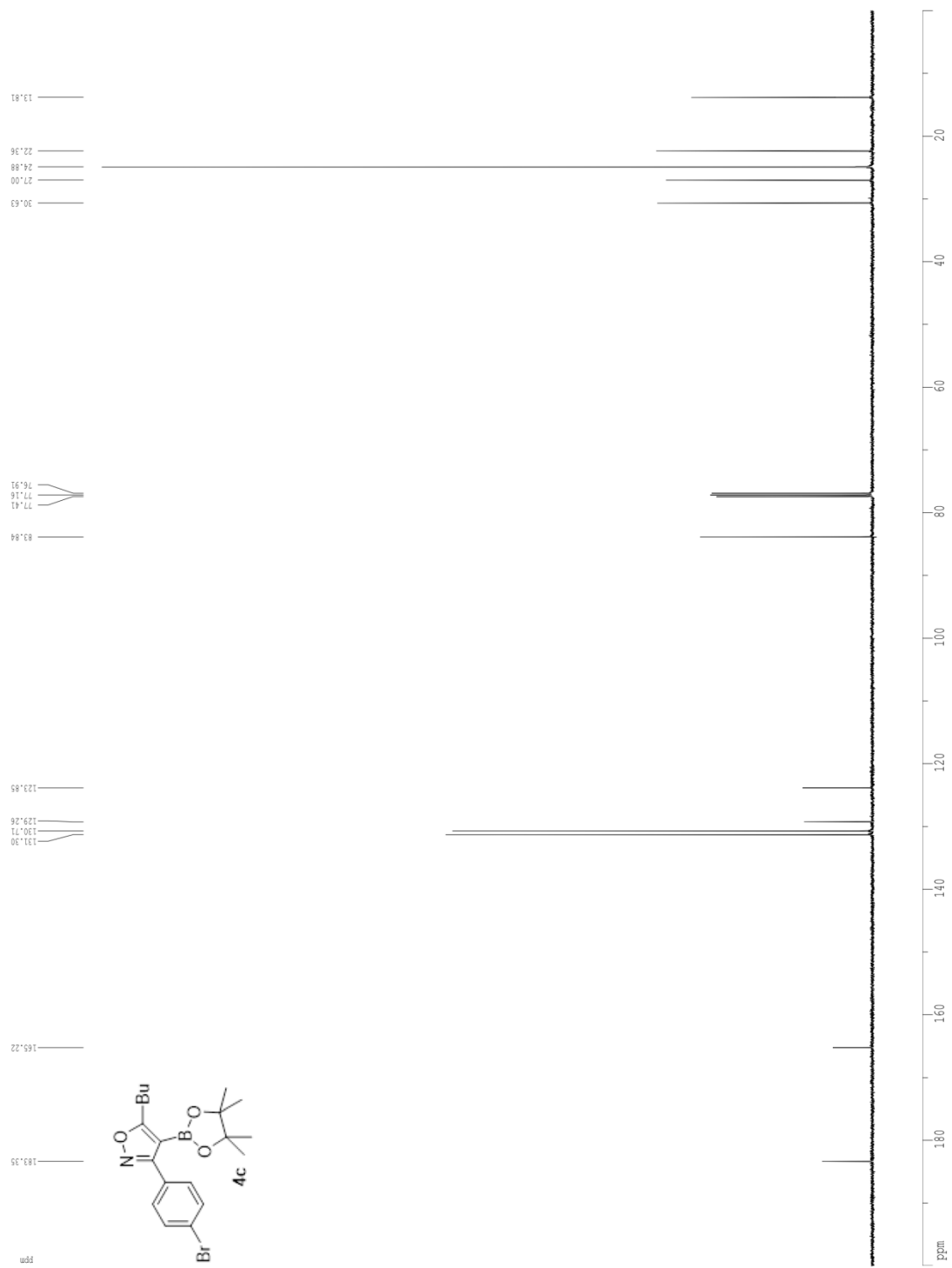


KT-II-031b (4c)  
11B spectrum using composite pulse for background suppression

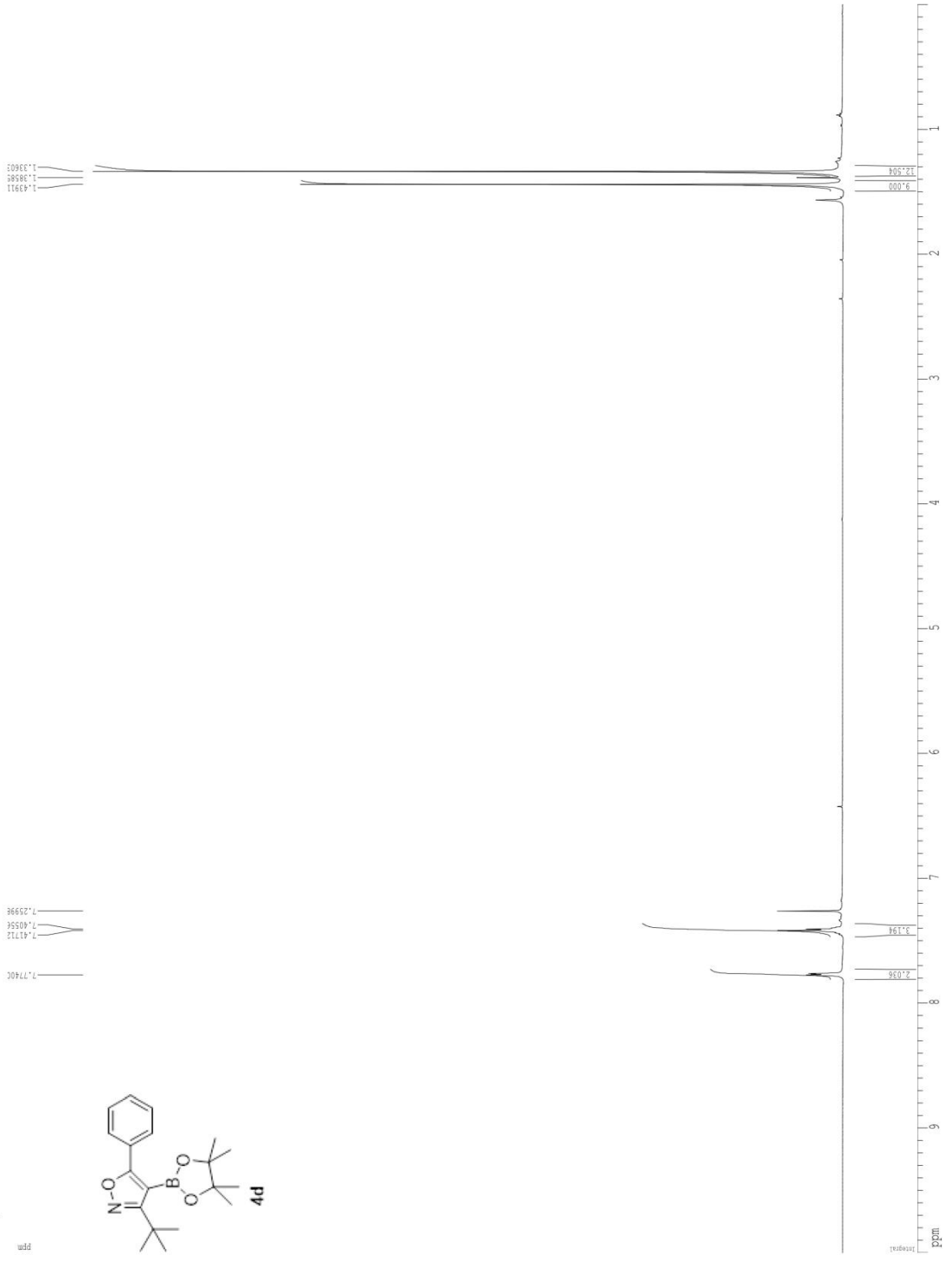
ppm



KT-II-031b (4c)  
Z-restored spin-echo 13C spectrum with 1H decoupling

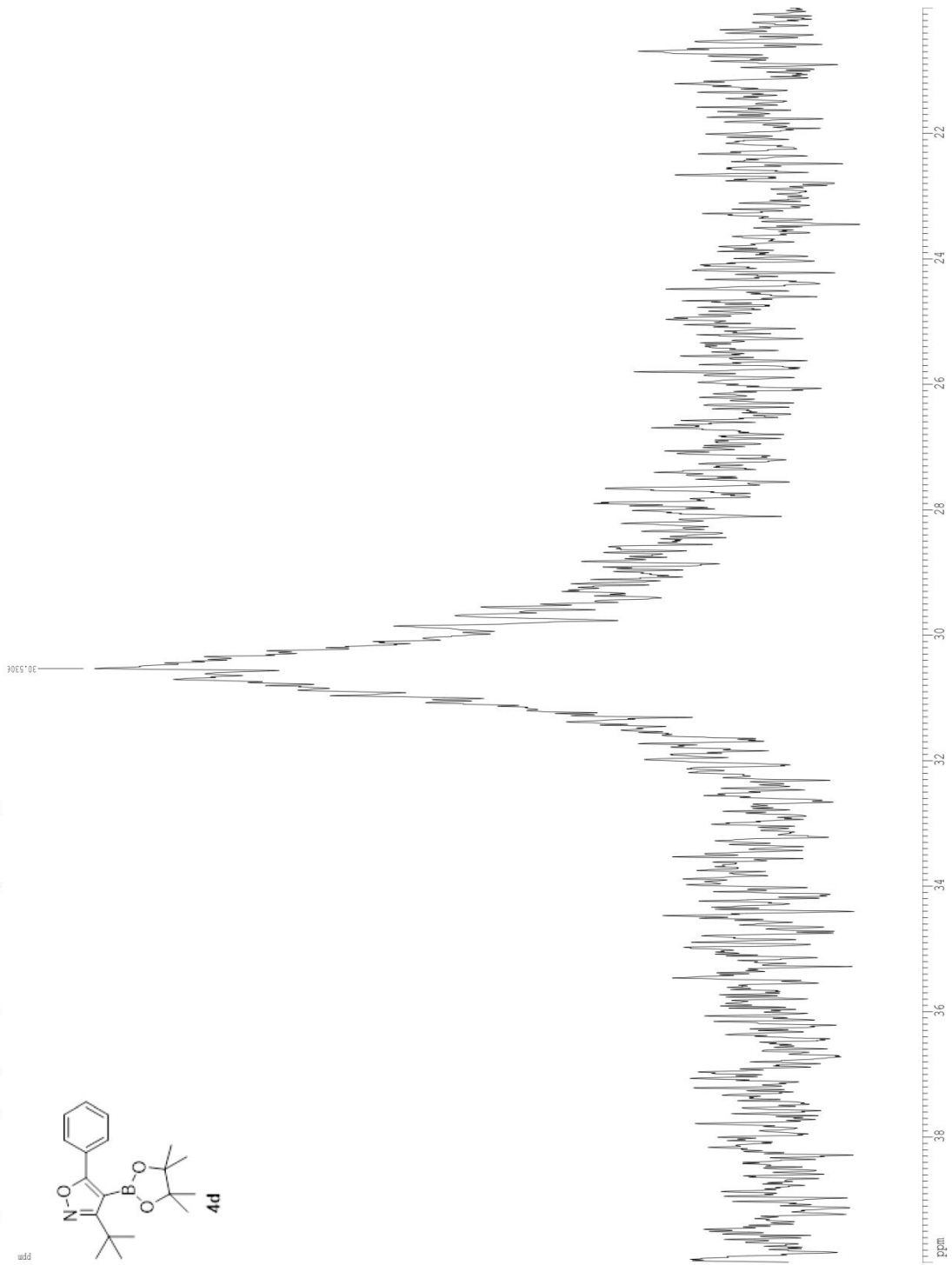
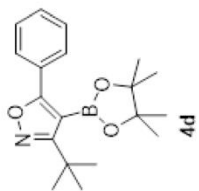


KT-II-039b (4d)  
 1H spectrum

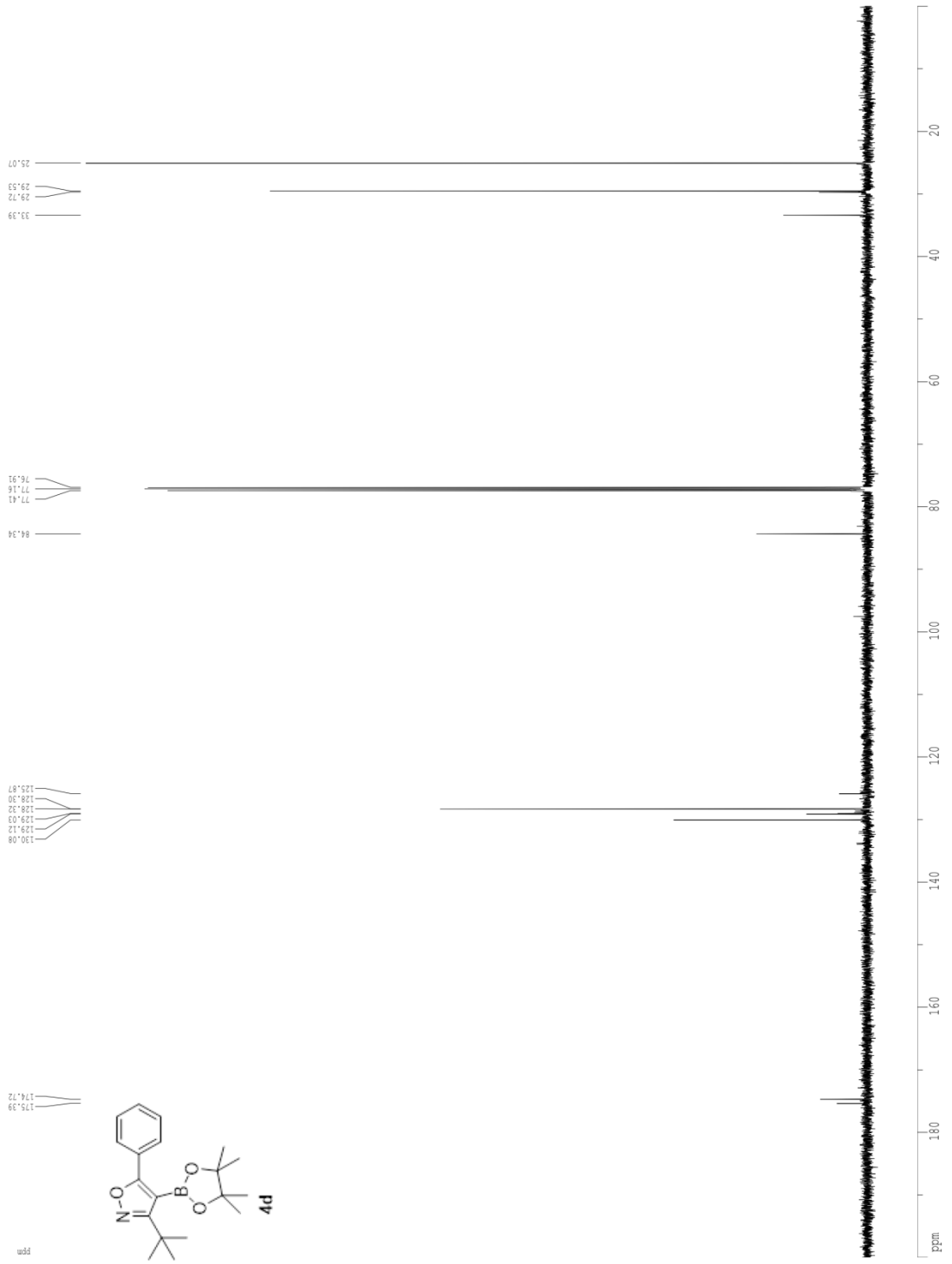


KT-II-039b (4d)  
11B spectrum using composite pulse for background suppression

ppm



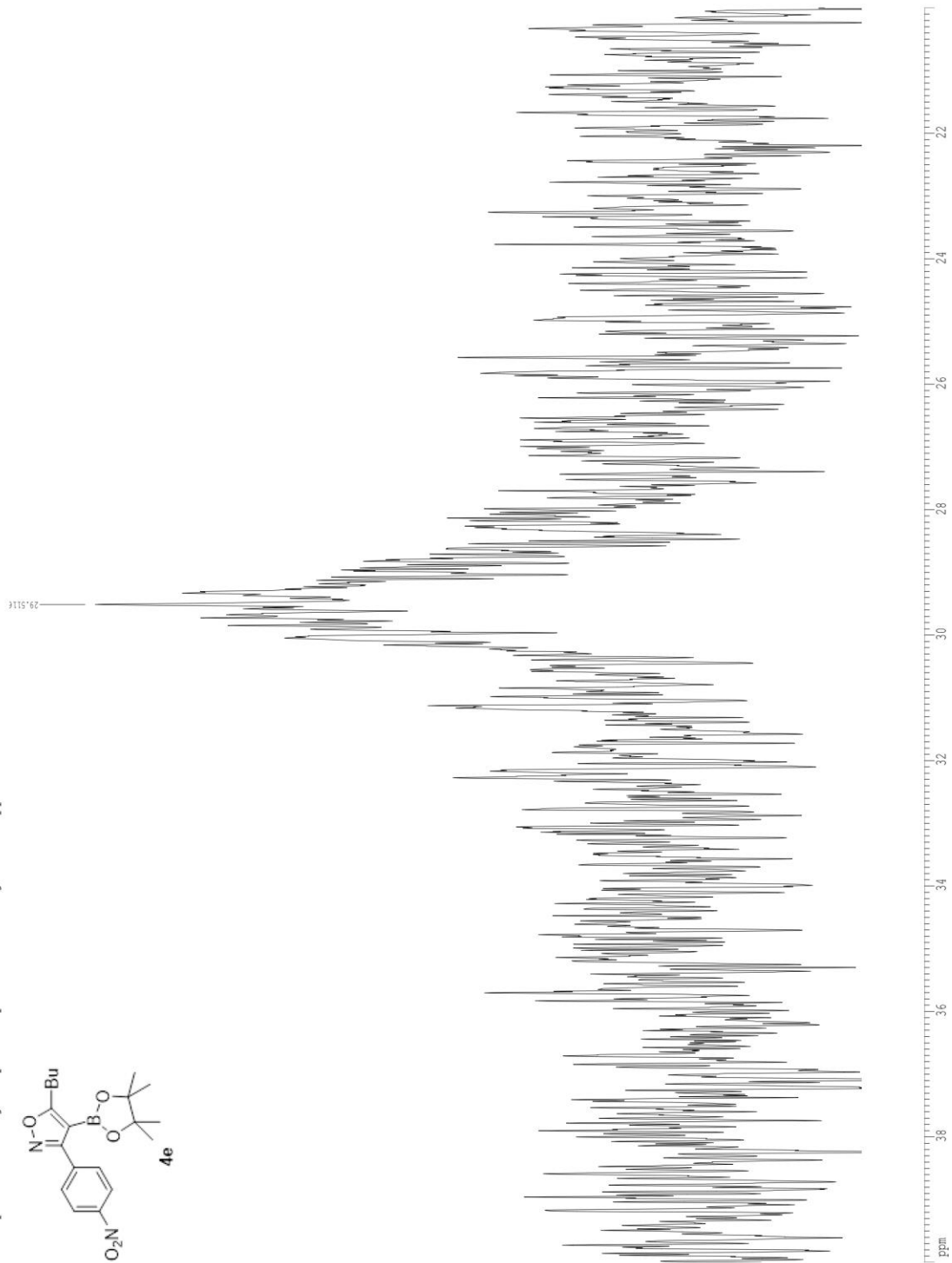
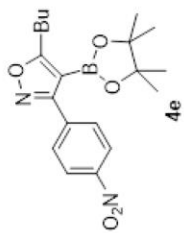
KT-II-039b (4d)  
Z-restored spin-echo 13C spectrum with 1H decoupling



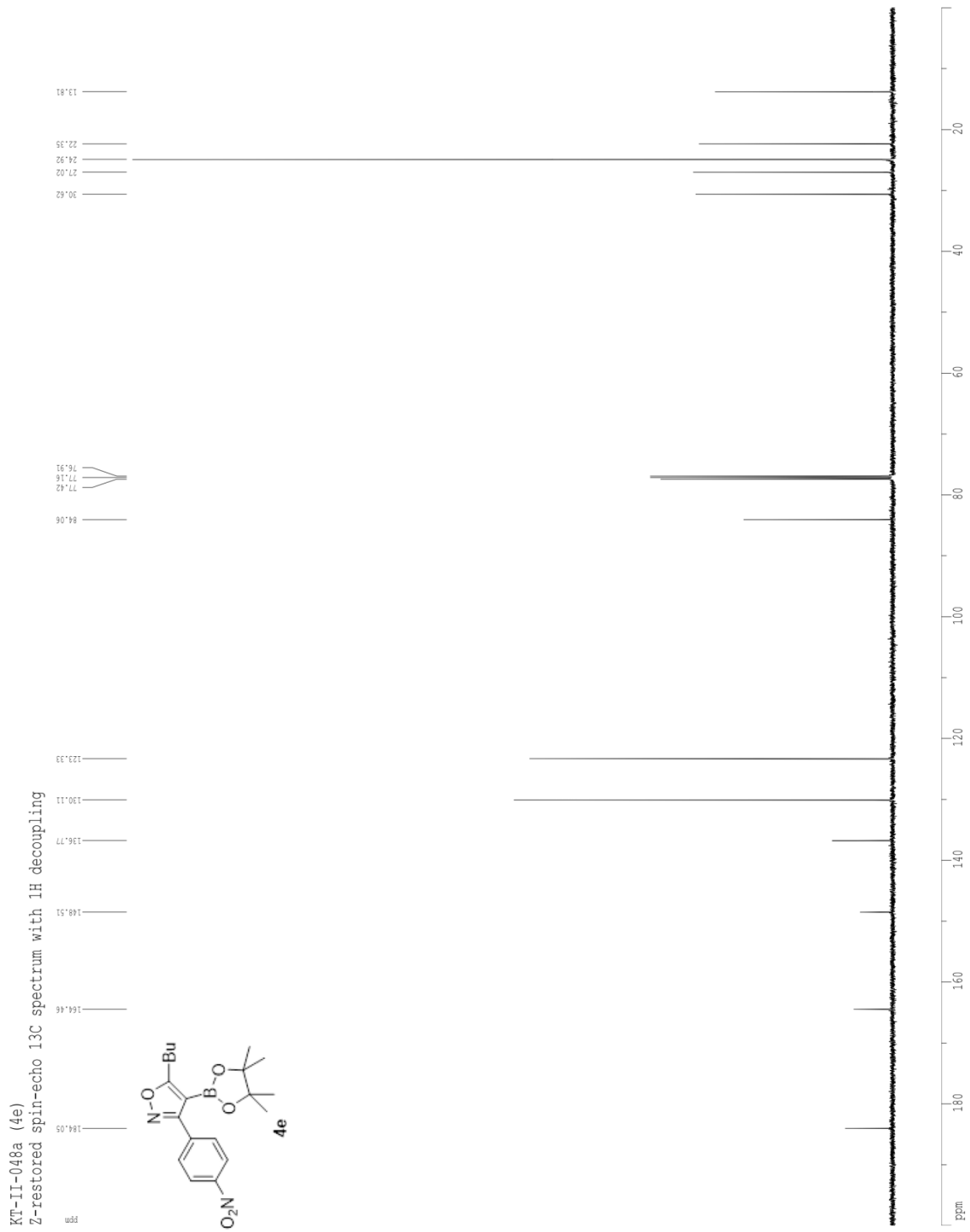
KT-II-048a (4e)  
1H spectrum



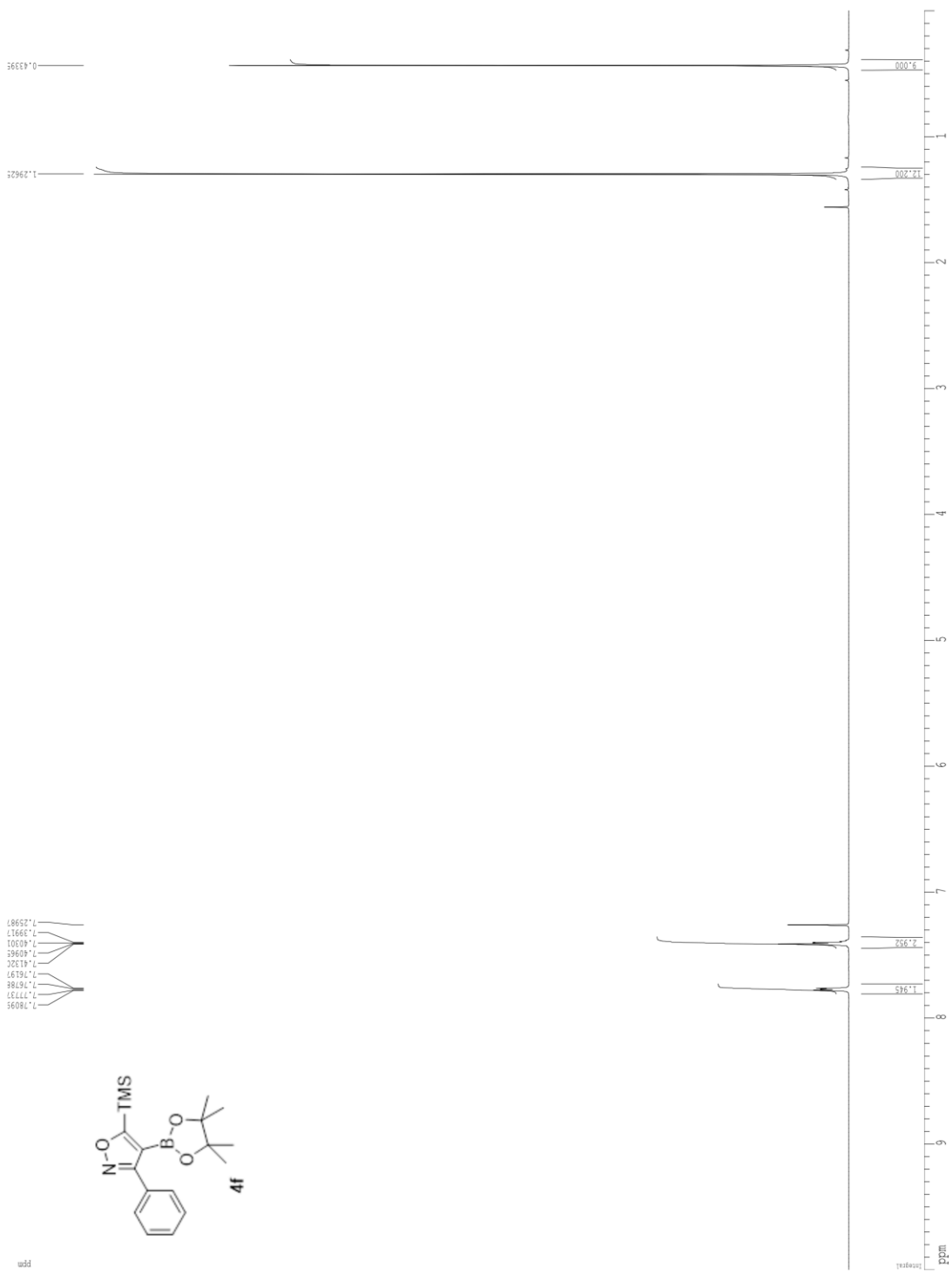
KT-II-048a (4e)  
11B spectrum using composite pulse for background suppression





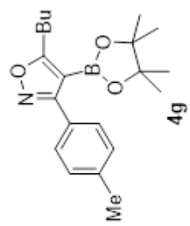


KT-II-112a (4f)  
1H spectrum

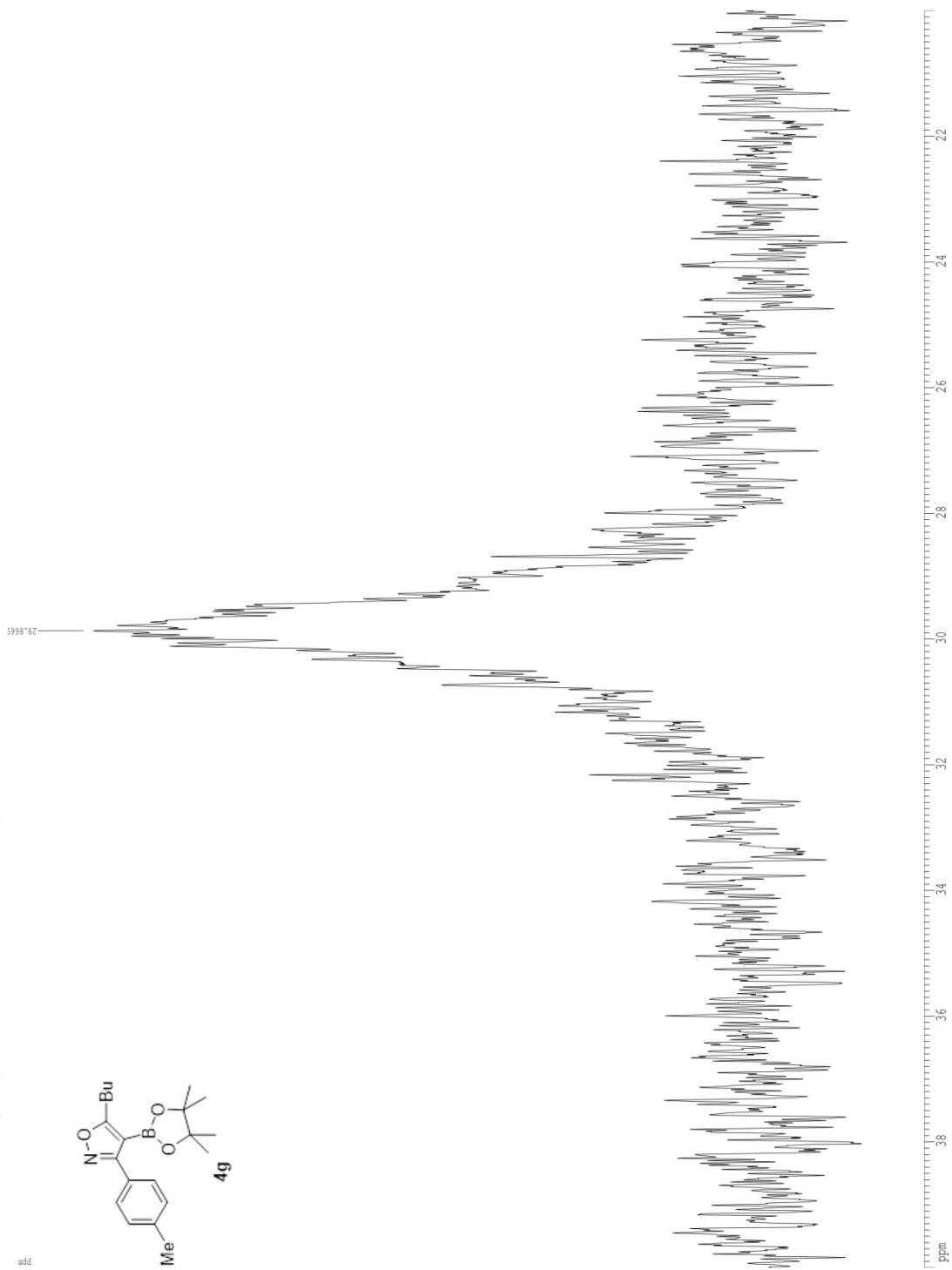


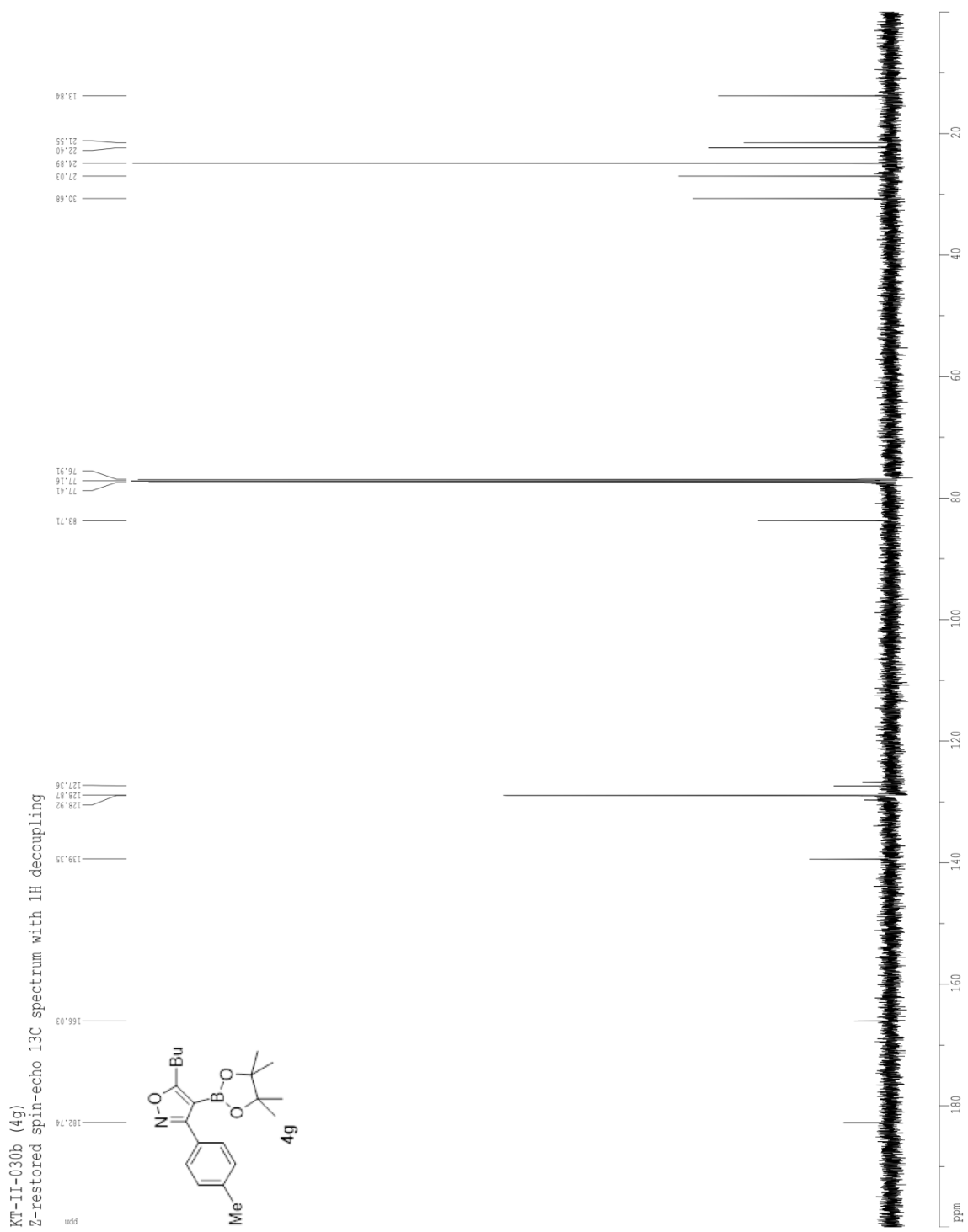
KT-II-030b (4g)  
1H spectrum

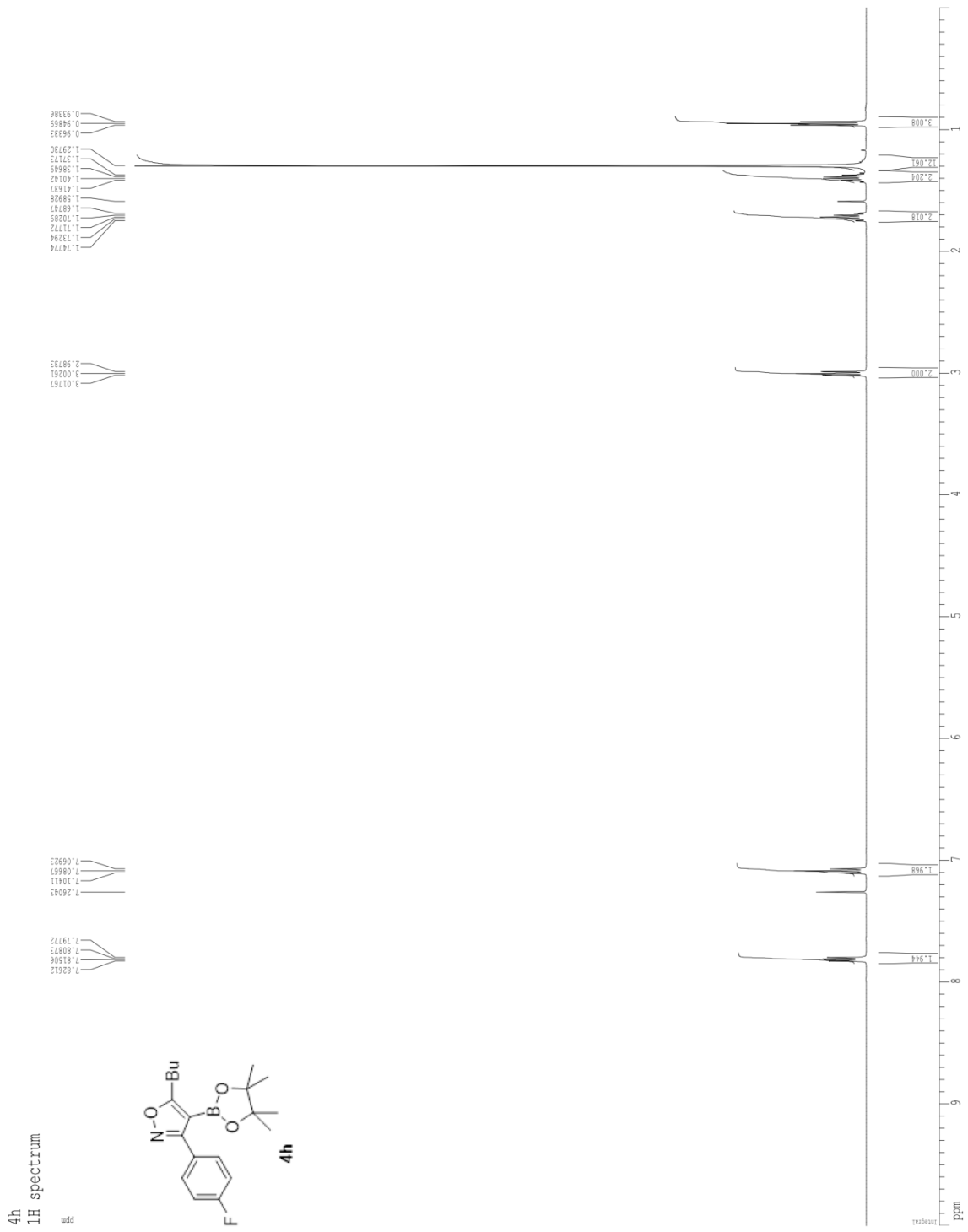
ppm



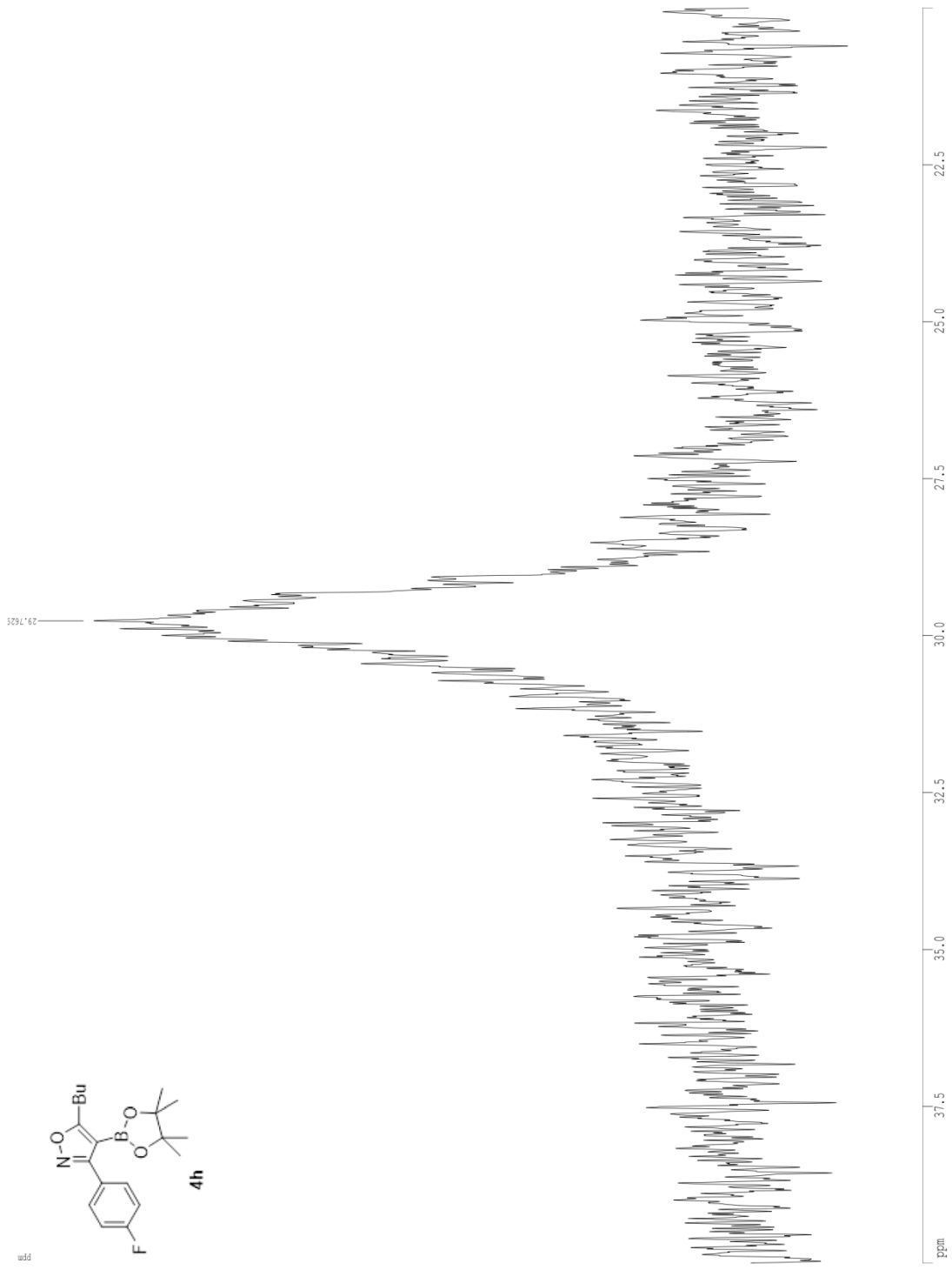
KT-II-030b (4g)  
11B spectrum using composite pulse for background suppression

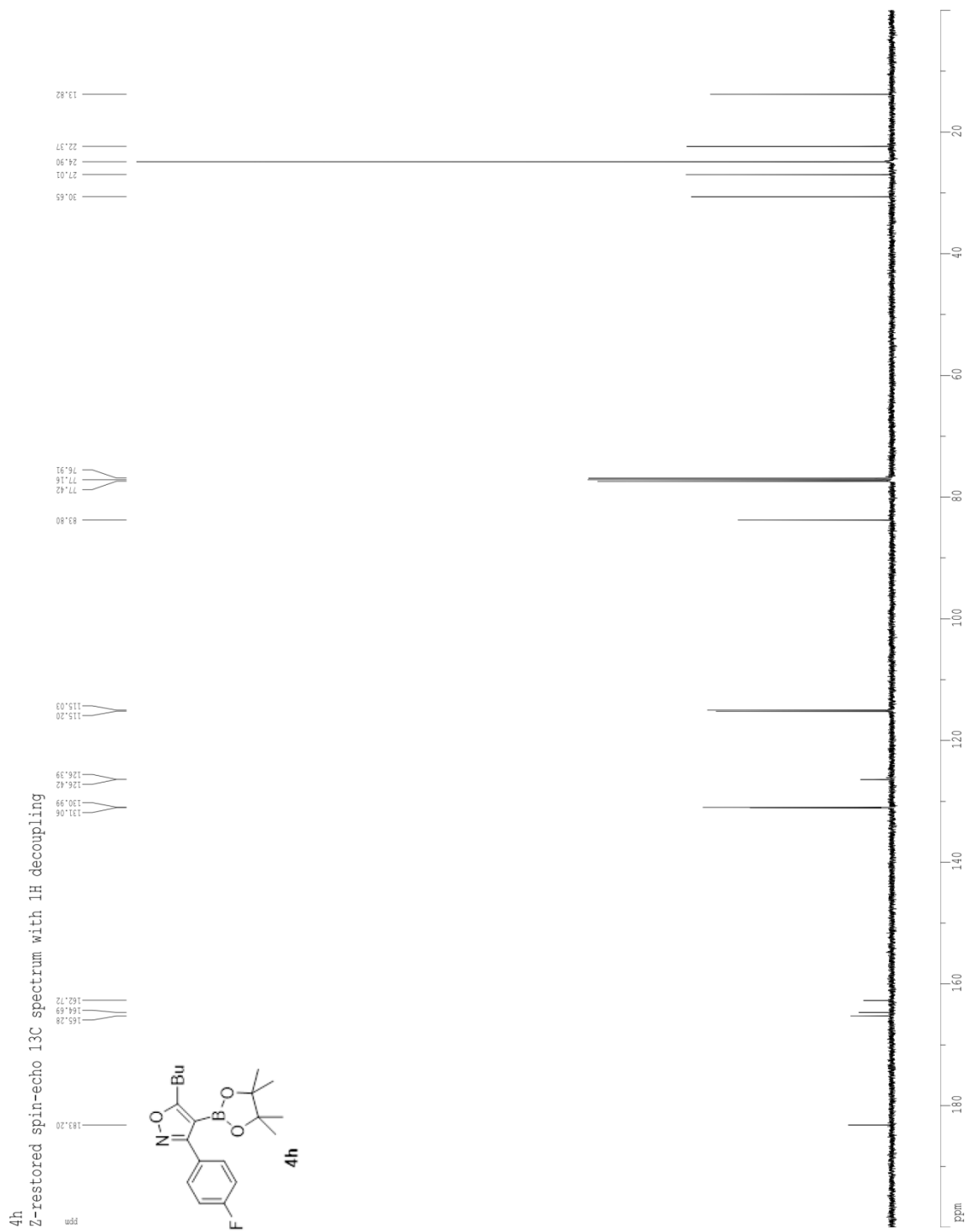






KT-I-151b (4h)  
11B spectrum using composite pulse for background suppression

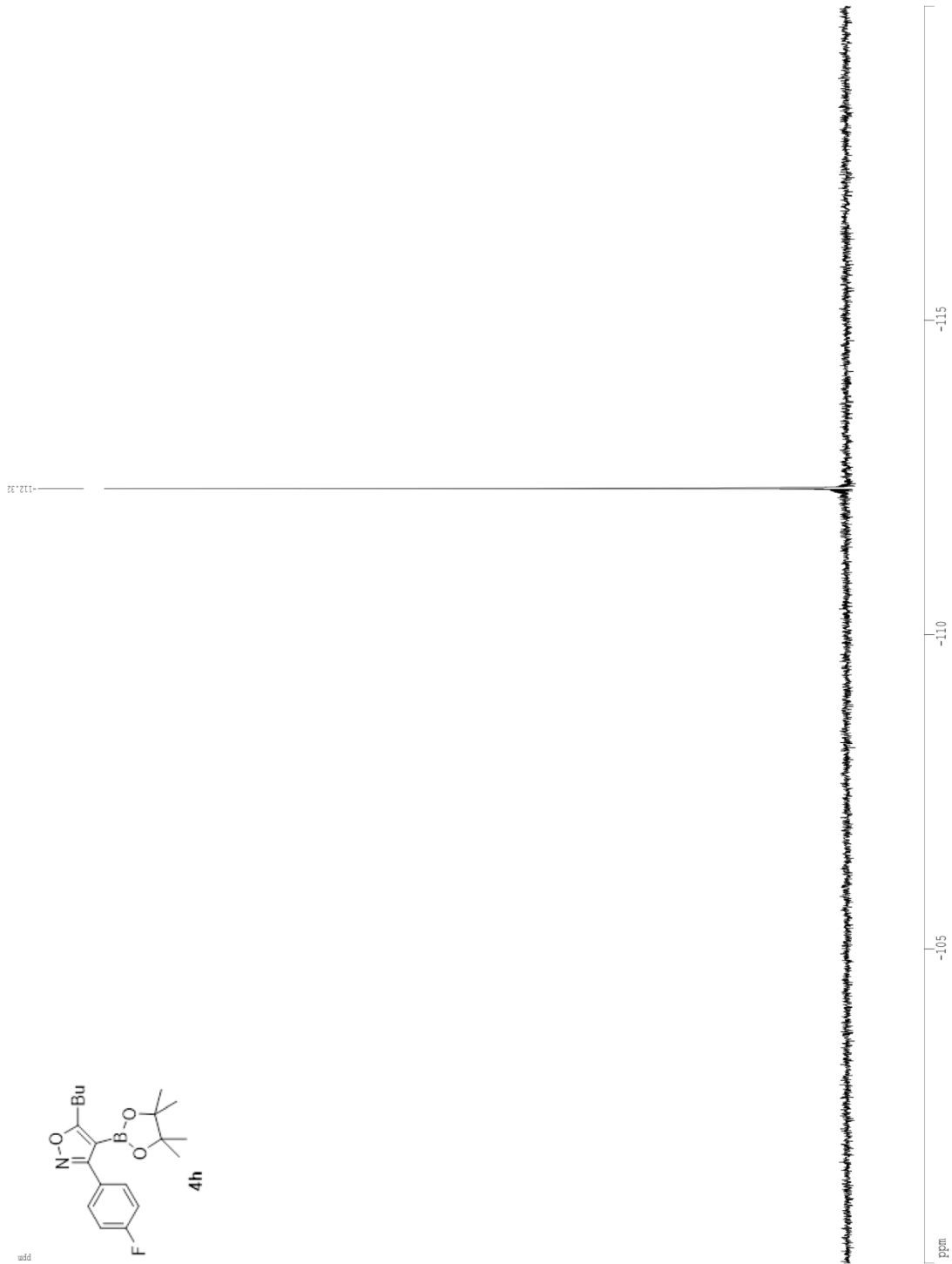
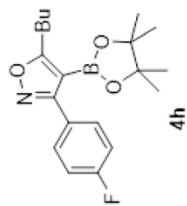




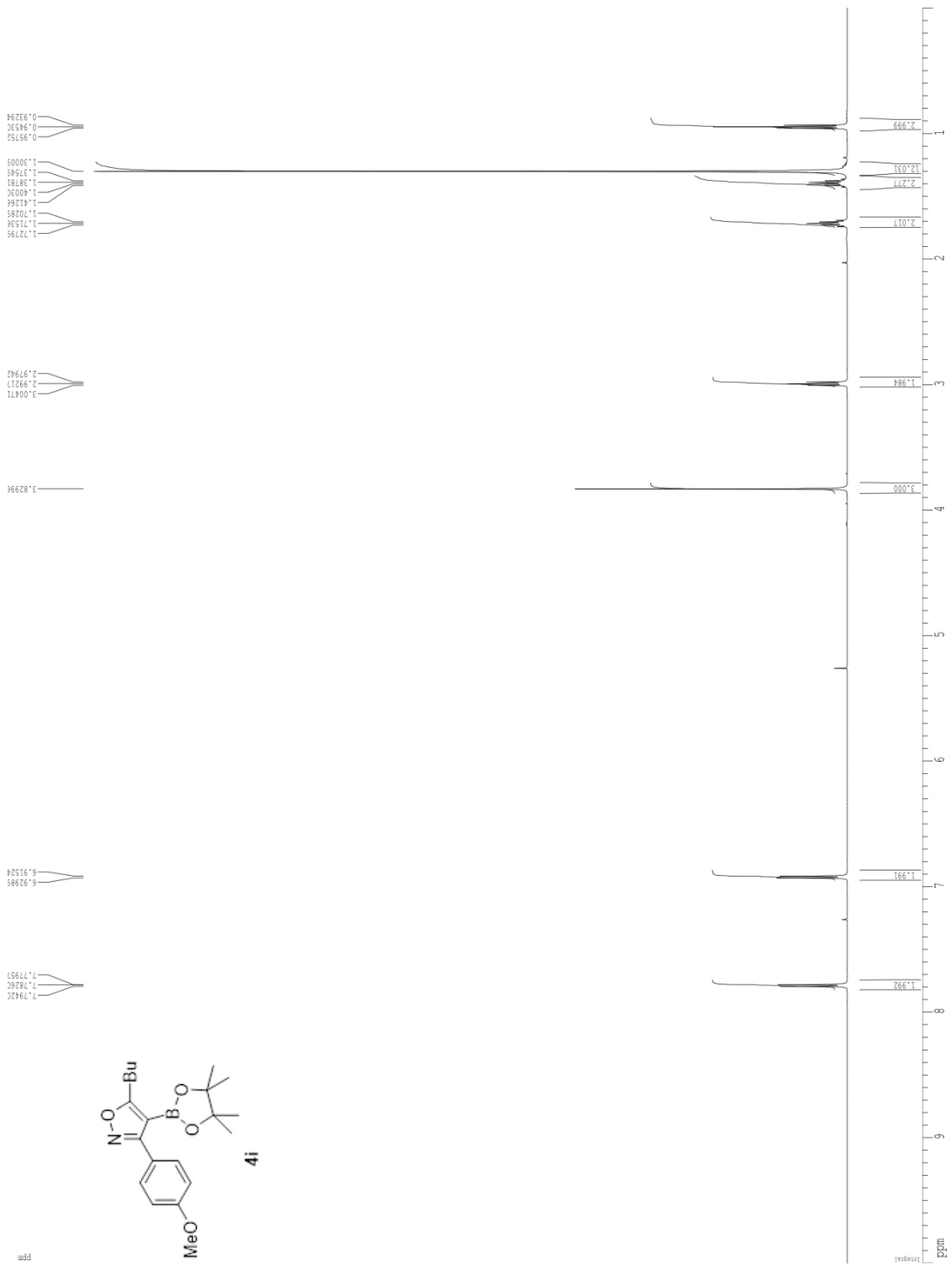


KT-I-151b (4h)  
19F spectrum with 1H decoupling

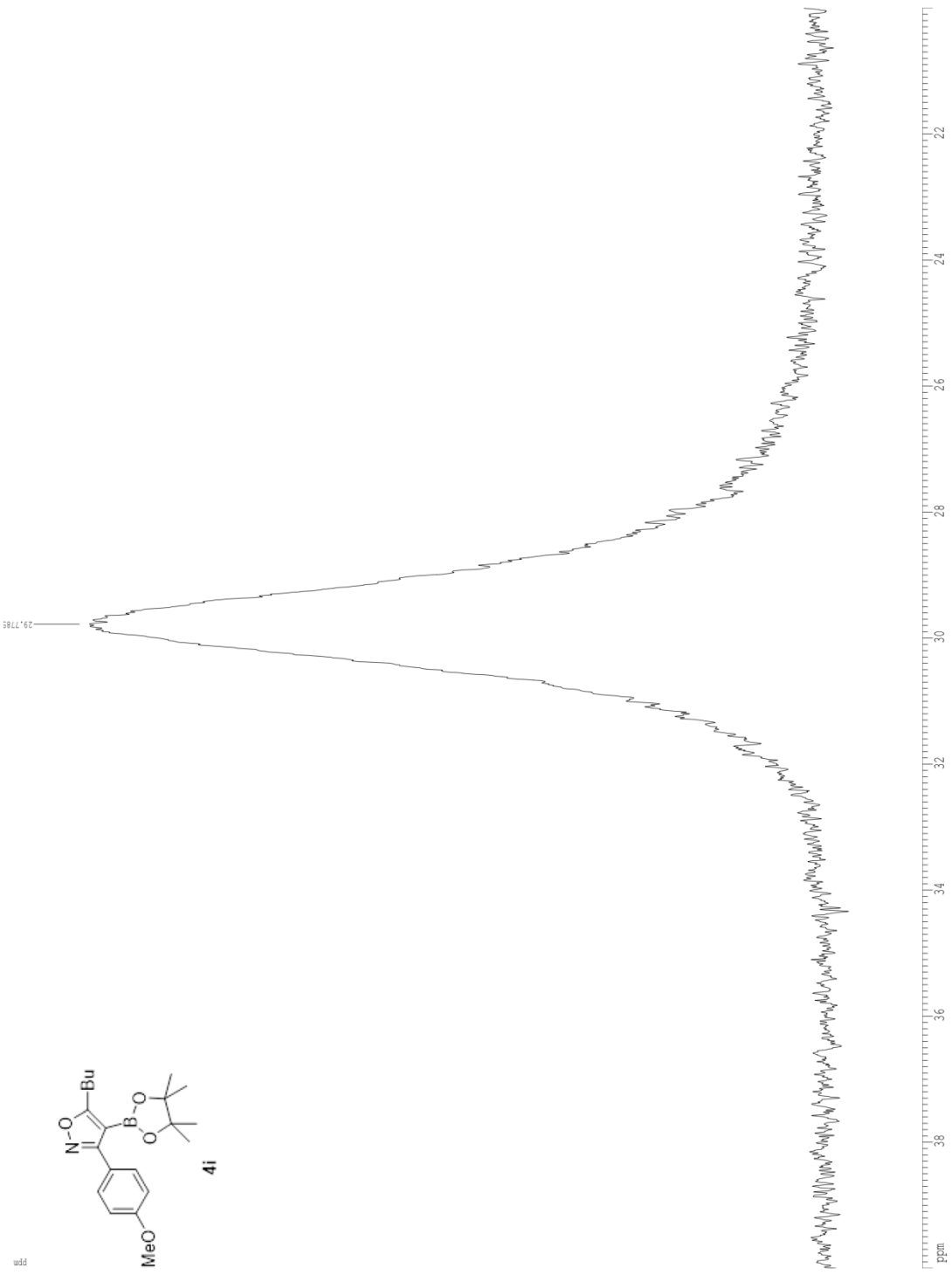
ppm



KT-II-047a (4i)  
 1H spectrum



KT-II-047a (4i)  
11B spectrum using composite pulse for background suppression



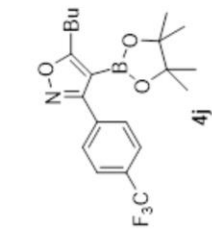
KT-II-047a (4i)  
Z-restored spin-echo 13C spectrum with 1H decoupling



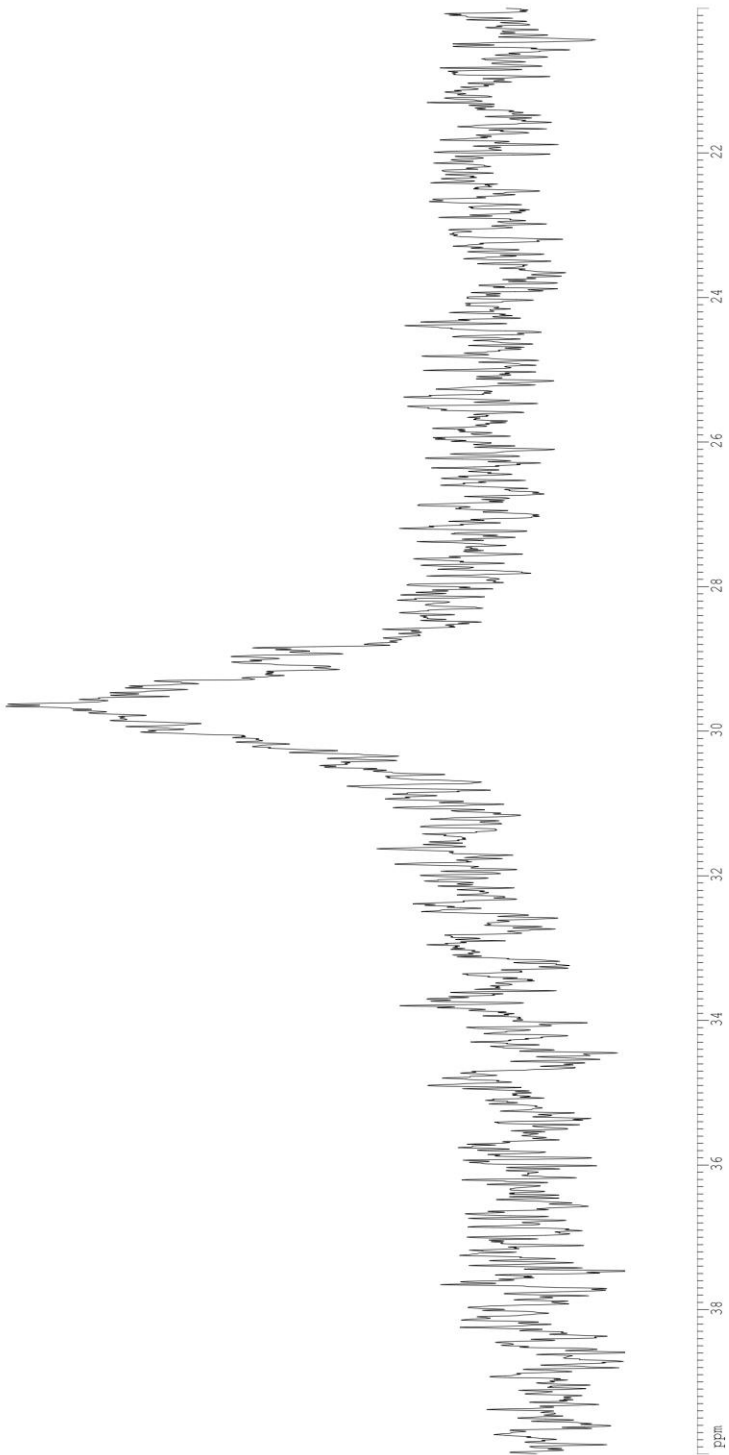
KT-3099  
<sup>1</sup>H spectrum



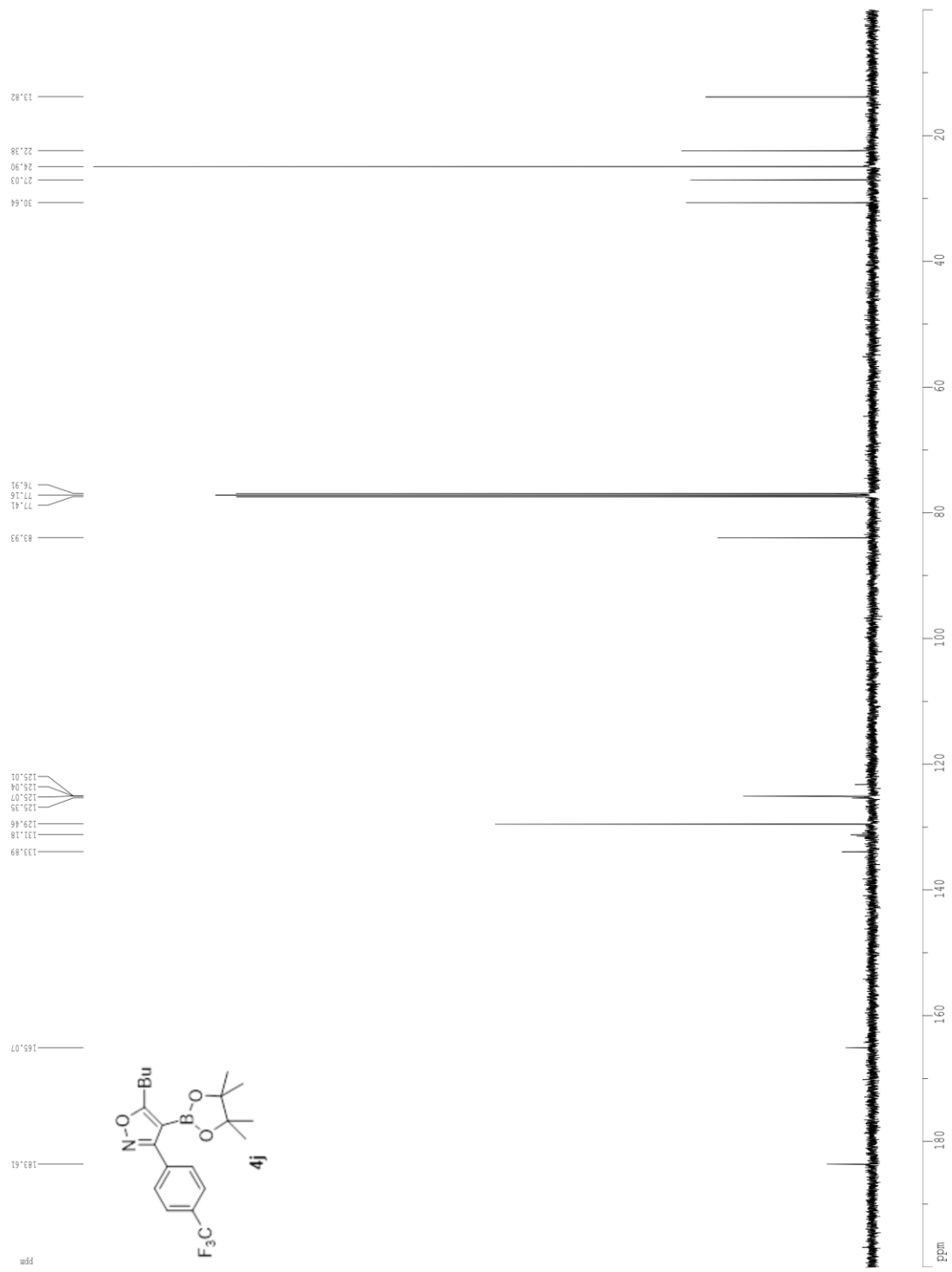
KT-3099  
11B spectrum



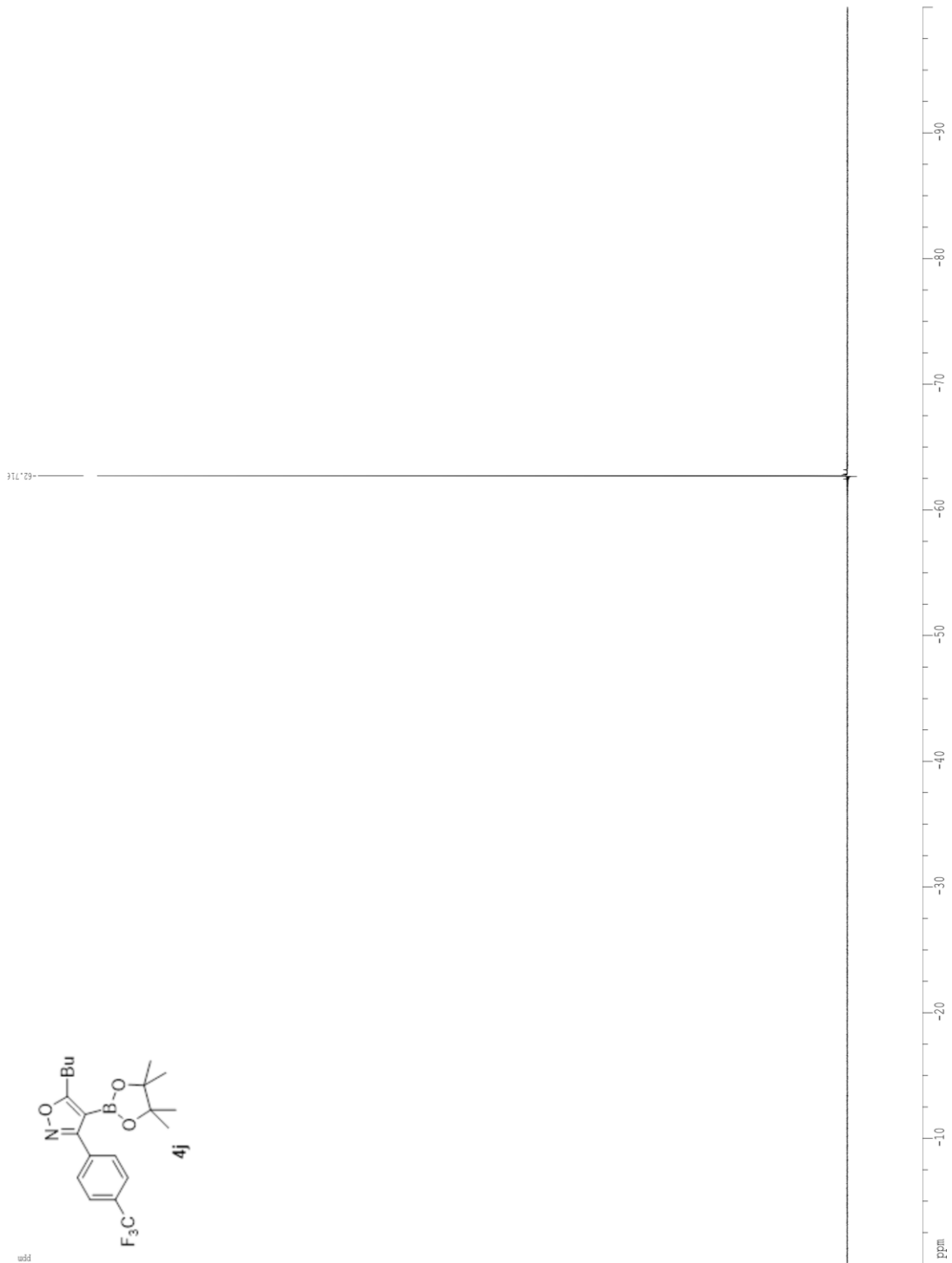
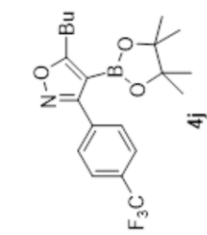
29.6525



KT-3099  
Z-restored spin-echo 13C spectrum with 1H decoupling

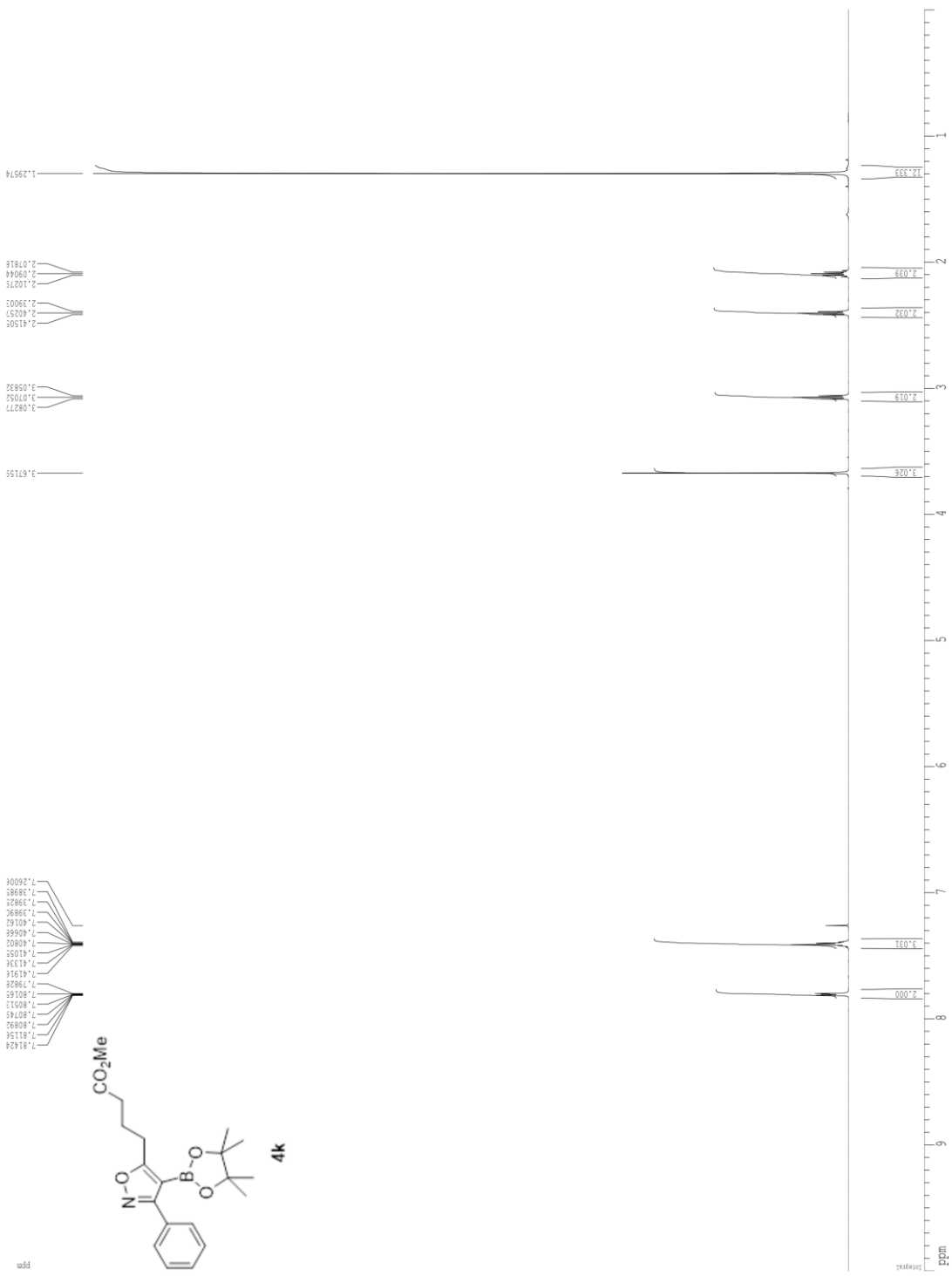


KT-3099  
19F spectrum with 1H decoupling

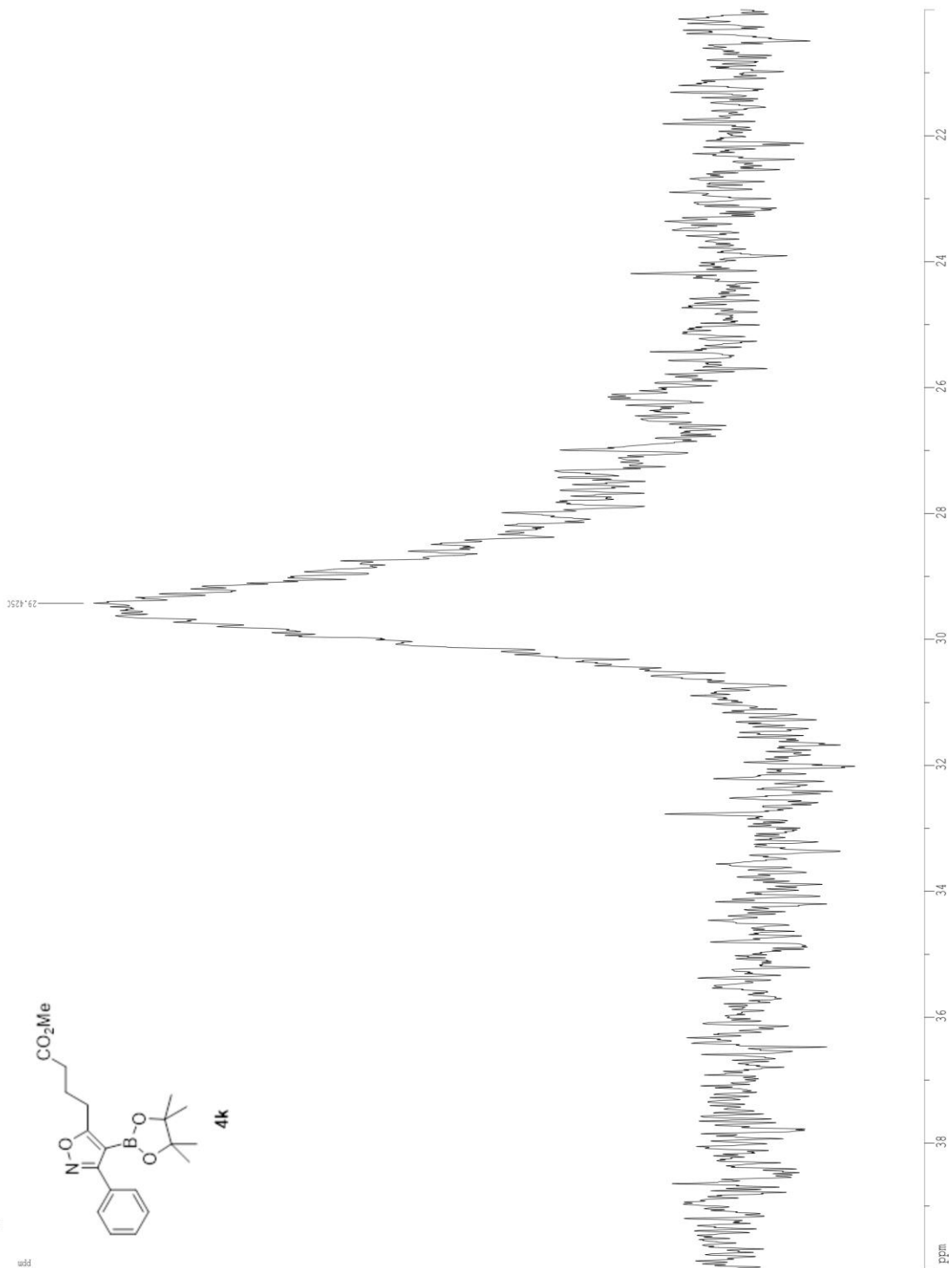
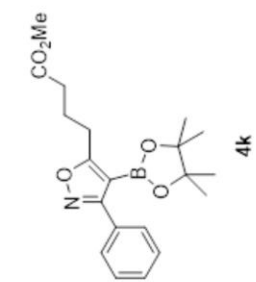




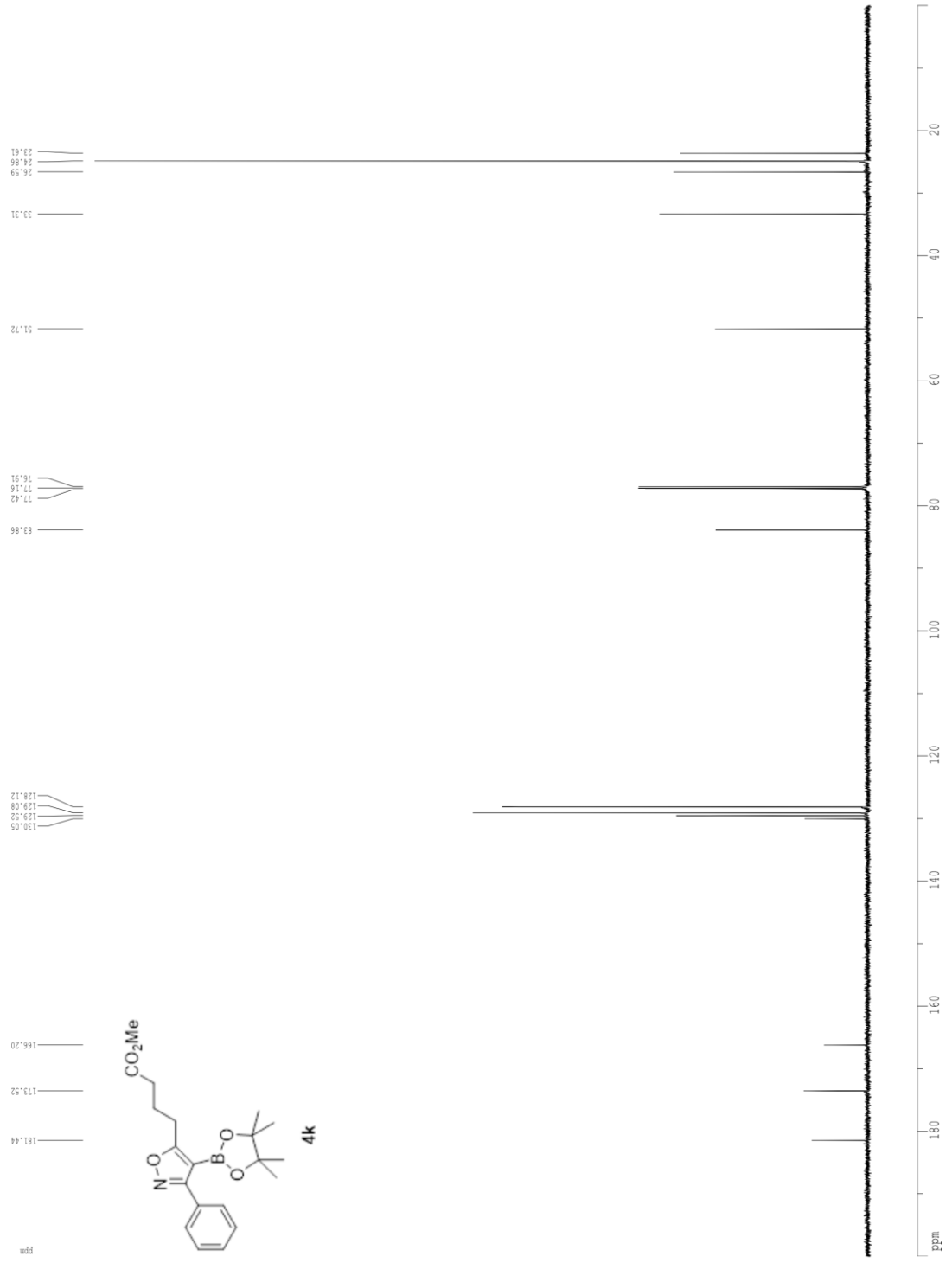
KT-3101  
1H spectrum

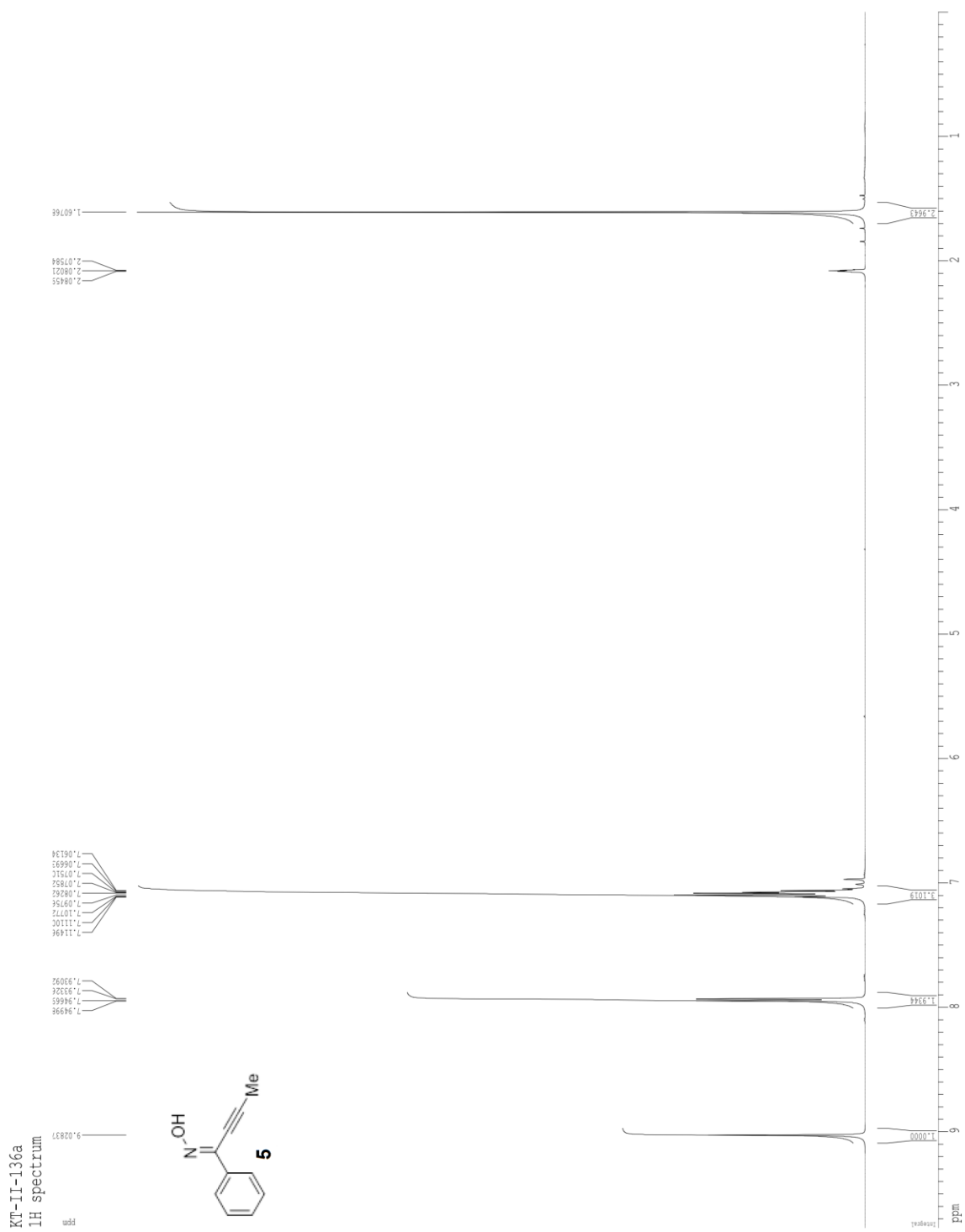


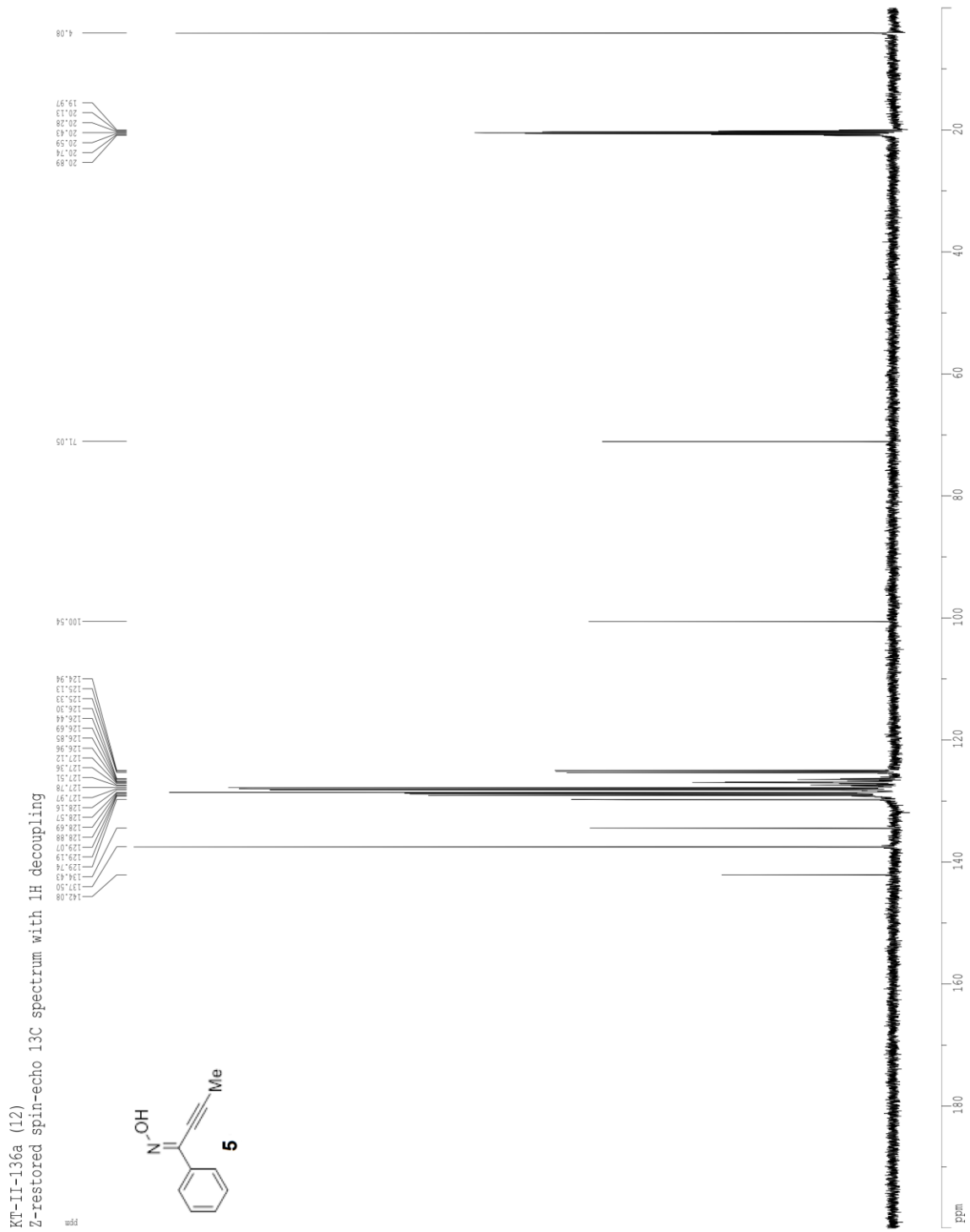
KT-3101 (4k)  
11B spectrum



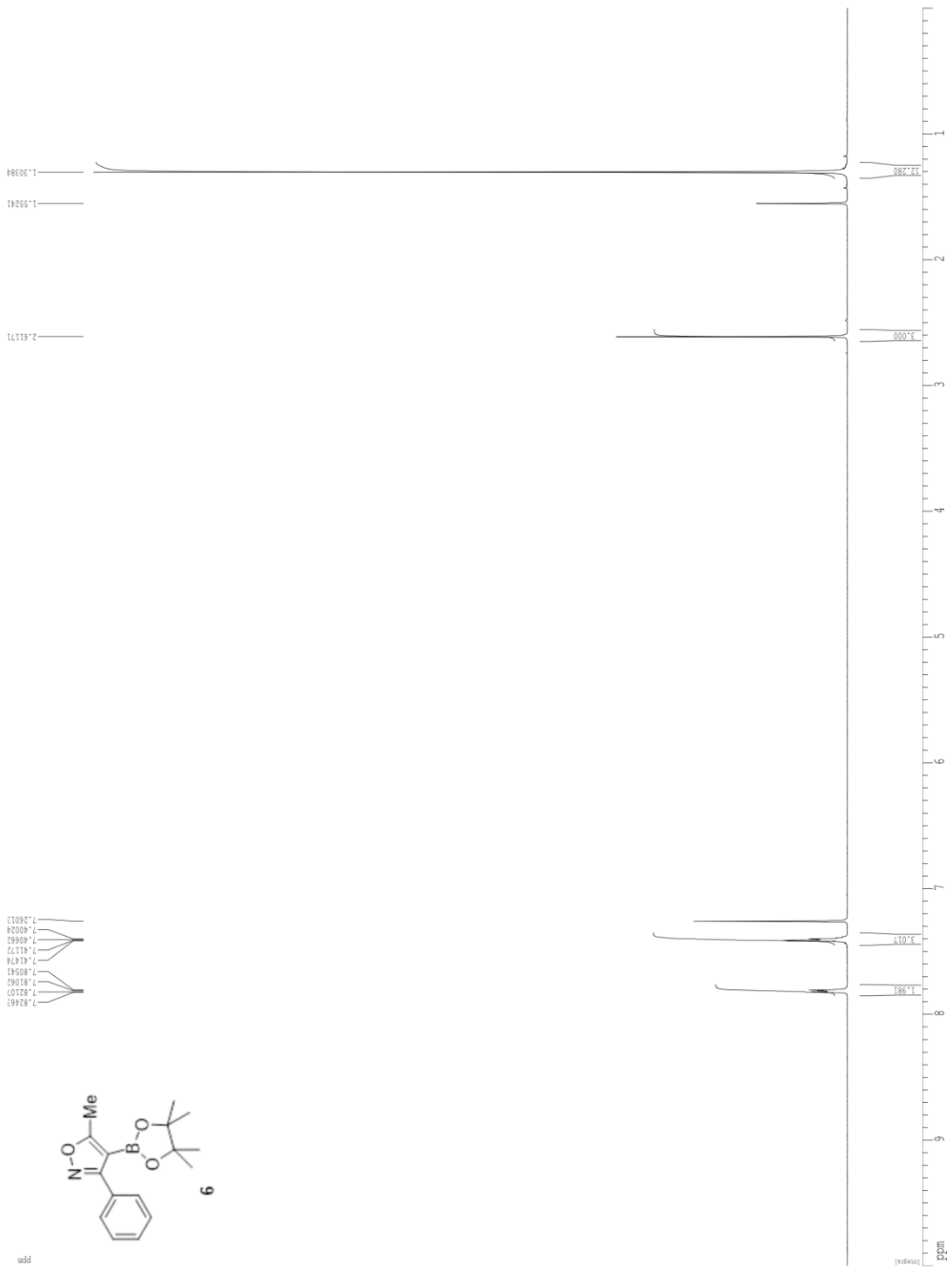
KT-3101  
Z-restored spin-echo 13C spectrum with 1H decoupling







KT-II-159b (6)  
1H spectrum



KT-3104a  
1H spectrum

